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Preparation and Complex Formation of Polymers Anchoring 2-Oxazolidinone

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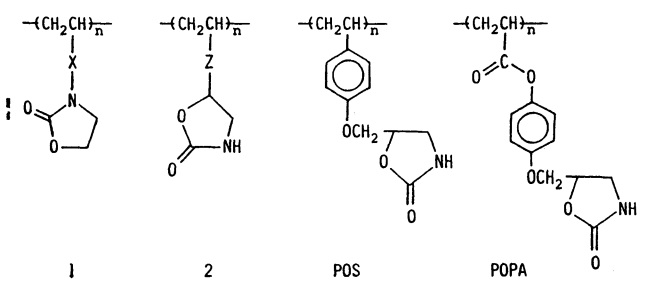
(Received March 18, 1988)

Polymers anchoring 3-unsubstituted 2-oxazolidinone were prepared and their complex formation with phenol and mercury(II) acetate were investigated. Preformed poly(4-hydroxystyrene) was treated with tris(2,3-epoxypropyl) isocyanurate to give a polymer containing 2-oxazolidinone residues within the limits of 57.7 mol%. Polymers carrying 2-oxazolidinone were also prepared through the homopolymerization and copolymerization of 4-(2-oxo-5-oxazolidinylmethoxy)phenyl acrylate. The effective concentration of 2-oxazolidinone residue in the polymers, which is accessible to phenol, was determined on the assumption that the polymer-bound 2-oxazolidinone and phenol formed a 1 : 1 complex. 2-Oxazolidinone and a mercury atom formed a 2 : 1 complex; this relation on the molar ratio applies to all forms of complexes between the mercury atom and the 2-oxazolidinone residue in the polymers.

2-Oxazolidinone has a reactive carbamoyl group, and its reactions lead to the formation of various useful compounds such as biocides,[1] surface active agents,[2] reactive reagents,[3] and reaction intermediates.[4] Polymers containing 2-oxazolidinone residues have also been reported. Walls and co-worker[5] previously noted that poly(3-vinyl-5-methyl-2-oxazolidinone) absorbed phenol, alkyl halides, and halogens. The complexes between 5-alkyl-3-vinyl-2-oxazolidinones and chlorine are useful as bactericides, fungicides, and bleaches.[6] Further, we have reported that a polymer containing 2-oxazolidinone rings in the main chain, prepared from 2,4-diisocyanatotoluene and 1,4-bis(2-oxo-5-oxazolidinylmethoxy)benzene, formed complexes with phenol and halogens.[7] Okawara and co-workers[8] have reported on a complex formation between tin(II) chloride and 2-oxazolidinone or 3-glycidyl-2-oxazolidinone; however, a complex of the salt with the polymer obtained from the latter compound is not examined in its paper. We have discovered the fact that a precipitate is formed when treating 2-oxazolidinone with mercury(II) acetate in methanol. This is, presumably, a complex between 2-oxazolidinone and mercury(II) acetate; its structure has been confirmed in this present work. Most of the polymers anchoring 2-oxazolidinone studied until now were of polymer type **1**:[5,8-12] almost no polymers in which a nitrogen atom adjacent to a carbonyl group holds a reactive hydrogen, such as polymer **2**, has been reported, except for poly(5-vinyl-2-oxazolidinone).[13] Polymer **2** must be capable of a complex formation with phenol and mercury(II) acetate. In this paper, therefore, we also report on the syntheses and complex formations of new polymers, poly[4-(2-oxo-5-oxazolidinylmethoxy)styrene](POS) and poly[4-(2-oxo-5-oxazolidinylmethoxy)phenyl acrylate](POPA), owing to interest in the characteristic properties of polymer-bound 3-unsubstituted 2-oxazolidinone (polymer **2** type). This work gives fundamental information on the use as carriers for biocides, as ligands for a polymer-metal complex catalyst, and as agents for heavy metal ions recovery in solutions.



Experimental

Materials. Poly(4-hydroxystyrene)(PHS) was purchased from the Maruzen Petrochemical Corp., $\overline{M}_w$ 5850, $\overline{DP}$ 49, hydroxyl equivalent 120, and $[\eta]$ 0.0906 dl g^{-1} (at 30 °C in DMSO). Tris (2,3-epoxypropyl) isocyanurate (TEPIC) was offered by the Nissan Chemical Corp. and was recrystallized from methanol, mp 102—104 °C (lit,[14] 103—104.5 °C). Acryloyl chloride was distilled prior to use. 5-(4-Hydroxyphenoxymethyl)-2-oxazolidinone was prepared from hydroquinone and TEPIC in a way similar to that mentioned in a previous paper.[6] 3-Phenylcarbamoyl-2-oxazolidinone was prepared from 2-oxazolidinone and phenyl isocyanate according to a previously published report.[15] 3,5-Diphenyl-2-oxazolidinone was prepared from styrene oxide and phenyl isocyanate.[16] 5-Phenoxymethyl-2-oxazolidinone (2-oxo-5-oxazolidinylmethoxybenzene, abbreviated to OMB), was prepared from phenol and TEPIC.[17] Solvents were dried and distilled before use. Other chemicals of reagent grade were used without further purification.

General Procedure for Reaction of PHS with TEPIC. A 300 cm^3, four-necked round-bottomed flask equipped with a stirrer, reflux condenser, and thermometer was charged with the desired amount of PHS, TEPIC, sodium hydroxide, and DMF. The reaction mixture was stirred at 158 °C for 7 h, followed by treating with phenol for 5 h. After evaporation of the solvent under reduced pressure, the residue was poured into water. The precipitate was washed with ethyl acetate, followed by reprecipitation from an acetone solution with water. The reprecipitate was washed with diethyl ether and dried under reduced pressure. The obtained content in 2-oxazolidinone residue in the polymers was determined by an

IR absorption analysis at 1740 cm^{-1}.

Synthesis of 4-(2-Oxo-5-oxazolidinylmethoxy)phenyl Acrylate (OPA). A 300-cm^3, round-bottomed flask equipped with a stirrer, reflux condenser, thermometer, and a inlet tube for nitrogen gas was charged with 3.5 g (0.017 mol) of 5-(4-hydroxyphenoxymethyl)-2-oxazolidinone and 150 cm^3 of tetrahydrofuran; then 1.5 g (0.17 mol) of acryloyl chloride and 2.4 g (0.023 mol) of triethylamine were added. After stirring under nitrogen for 3 h, the precipitate was removed by filtration. The filtrate was treated first with a 5% aqueous solution of sodium hydrogencarbonate, followed by two extractions using diethyl ether. The ether-layer was washed with water, and dried over anhydrous sodium sulfate, followed by distillation. The residue was recrystallized from ethanol. Yield 31.8%; mp 141—142 °C (colorless needle). Found: N, 5.18%. Calcd for $C_{13}H_{13}NO_5$: N, 5.32%. IR(KBr) 3270 (NH), 1750 (C=O), 1730 (C=O), 1630 (C=C), 1500, 1405, 1300, 1250, 1200, 1165, 1150, 825, and 805 cm^{-1}.

Procedure for Polymerization of OPA. OPA 0.8 g, 1,4-dioxane 6 cm^3 and 1 mol% AIBN were charged into a reaction tube. The mixture was treated at 50 °C under nitrogen in a sealed tube. After 24 h, the contents of the tube had gelled. The obtained polymer was washed with 1,4-dioxane and diethyl ether, followed by vacuum drying. Yield 86%.

Copolymerization with styrene was carried out in a way similar to the homopolymerization method. Yield 48.3%. The composition of the copolymer was determined by an elementary analysis. Found: C, 59.51; H, 5.32; N, 4.91%.

General Procedure for the Complex Formation between 2-Oxazolidinones and Phenol. The 2-oxazolidinones (200 mg) were added to 5 cm^3 of an aqueous solution of phenol; the specimens were kept at 30 °C with shaking. After 2 days, the solids were separated by filtration, and the concentration of phenol in the liquid phase was evaluated by measuring the absorption at 280 nm.

General Procedure for the Complex Formation between 2-Oxazolidinones and Mercury(II) Acetate. The 2-oxazolidinones (200 mg) were added to 10 cm^3 of 0.08×10^{-3} mol dm^{-3} aqueous solution of mercury(II) acetate, and the specimens were kept at 30 °C with shaking. After 2 days, the solids were separated by filtration; then, the amount of mercury(II) acetate in the liquid phase was determined by atomic absorption analysis.

Reaction of 2-Oxazolidinone with Mercury(II) Acetate in Methanol. 2-Oxazolidinone (1.51 g, 1.74×10^{-3} mol) was dissolved in 20 cm^3 of methanol. The solution was poured into a solution containing mercury(II) acetate (2.82 g, 8.84×10^{-3} mol) in 30 cm^3 of methanol. The mixture was permitted to stand overnight. The precipitate was collected by filtration. The filtrate was washed with methanol, and dried under reduced pressure. Yield 2.05 g (colorless needle); Atomic absorption analysis Hg 48.6%; ^1H NMR (DMSO-d_6) δ=4.30 (2H, t, CH_2) and 3.60 (2H, t, CH_2); For IR(KBr) see Fig. 5.

Results and Discussion

Preparation of POS and POPA. It has been reported that OMB[17] was obtained by treating phenol with TEPIC in the presence of sodium hydroxide. Previously, we had also succeeded in synthesizing 5-(4-hydroxyphenoxymethyl)-2-oxazolidinone[6] from hydroquinone and TEPIC. Therefore, the reaction of PHS with TEPIC was studied in order to prepare POS. PHS is prepared through a polymerization of 4-hydroxystyrene; however, the proportion of the side reaction, such as chain-transfer and termination, becomes higher with an increase in the degree of polymerization, and an insoluble polymer is finally formed. It was attributed to forming a cross-linked polymer caused by a chain-transfer to phenolic hydroxyl groups.[18] Therefore, though its molecular weight is low, a linear soluble PHS was used for the reaction with TEPIC, since the number of phenolic hydroxyl groups in the polymer can be accurately measured. The reaction was carried out under homogeneous conditions in DMF in the presence of sodium hydroxide. Unreacted TEPIC was transformed into OMB by treating with phenol; the produced OMB was removed from the reaction products through washing with ethyl acetate and reprecipitation. The IR spectra of the reaction products show two characteristic absorption bands at 3400 (O-H of phenol) and 1740 cm^{-1} (C=O of 2-oxazolidinone). If the reaction was completed, the absorption attributed to the O-H bond should disappear. The results of the IR spectra are, thus, indicative of the presence of unreacted phenolic hydroxyl groups. The content in 2-oxazolidinone residue in the polymers was determined spectrophotometrically by using the absorbance at 1740 cm^{-1} with 5-phenoxymethyl-2-oxazolidinone as a standard.

The results are summarized in Table 1. It was confirmed that the 2-oxazolidinone content for POS 3 is nearly equal to that determined by elementary analysis. In stoichiometric reactions between TEPIC and phenolic hydroxyl groups in the polymer, the 2-oxazolidinone content was a maximum value, and could not rise beyond 58%, despite long reaction times (14 hours) and the use of excess TEPIC. These results can be explained by suggesting that the polymer-bound 2-oxazolidinones surrounding fresh active phenolic oxygens hinder, to some extent, a further reaction of TEPIC with these phenolic active sites. However, the results shown in Table 1 suggest that the use of a smaller amount of TEPIC than the stoichiometric molar ratio allows the 2-oxazolidinone content in the polymer to be controlled. All these polymers were soluble in acetone, benzene, THF, DMF, and DMSO.

As previously described, significant amounts of the unreacted phenolic hydroxyl groups are present in the polymers anchoring 2-oxazolidinone, prepared from the preformed PHS. Therefore, a vinyl monomer containing a 2-oxazolidinone moiety, OPA, was preformed from 5-(4-hydroxyphenoxymethyl-2-oxazolidinone and acryloyl chloride, and was homo- and copolymerized in 1,4-dioxane by using AIBN as initiator. Little and Pickens[7] have reported that homopolymerization of 5-vinyl-2-oxazolidinone for a type-**2** polymer should be impossible, except for a copolymerization

Table 1. Preparation of the Polymers Anchoring 2-Oxazolidnone

Abbreviation[a]	Material[b] mole ratio	Reaction condition[c]			Product		
		Solvent	Time h	Temp °C	Yield %	$[\eta]$[d] dl g^{-1}	2-Oxazolidinone residue in the polymers/mole fraction
PHS	HSU=1	—	—	—	—	0.0906	0.000
POS 1	HSU/TEPIC=3.0	DMF	7	158	72.9	0.0710	0.577
POS 2	HSU/TEPIC=4.5	DMF	7	158	82.3	0.0814	0.506
POS 3	HSU/TEPIC=9.0	DMF	7	158	83.8	0.0849	0.282
POPA	OPA=1	Dioxane	24	50	76.7	insoluble[e]	1.000
OPA-St	OPA/St=1	Dioxane	24	50	48.3	soluble[e]	0.850

a) PHS: Poly(4-hydroxystyrene); POS: Poly[4-(2-oxo-5-oxazolidinylmethoxy)styrene] prepared from PHS; POPA: Homopolymer of 4-(2-oxo-5-oxazolidinylmethoxy)phenyl acrylate(OPA); OPA-St: Copolymer of OPA and styrene (St). b) HSU: Constitutional repeating unit in PHS; TEPIC: tris(2,3-epoxypropyl) isocyanurate. c) In the presence of ca. 4 mol% NaOH for POS 1, 2, and 3; used AIBN as an initiator for POPA, and OPA-St. d) Measured at 30 °C in DMSO. e) In DMF, DMSO, and NMP.

with methyl methacrylate. However, the monomer OPA obtained in this paper did homopolymerize, and gel. Homopolymerization gave a 86% conversion. The OPA-homopolymer (POPA) was swollen by, but insoluble in, pyridine, *m*-cresol, DMF, DMSO, and NMP, in contrast to water soluble poly(3-vinyl-2-oxazolidinone).[10] On the other hand, the equimolar reaction between OPA and styrene gave a copolymer (OPA-St) containing 15 mol% styrene, and it can be seen that the reactivity for OPA was higher than that for styrene. However, this should be judged more exactly on the basis of a reactivity ratio determination for OPA and styrene. The obtained copolymer was soluble in the solvents mentioned above.

Complex Formation of the Polymer-Bound 2-Oxazolidinone with Phenol. Several types of polymer-bound 2-oxazolidinone were incubated with an aqueous solution of phenol at 30 °C for 2 days. In confirmation of the attainment of equilibrium, several phenol determinations were performed after 2 and 7 days incubation: both values were identical.

The results were analyzed by applying an equation which Komiyama and co-workers[19] proposed for the complex formation between a β-cyclodextrin residue in immobilized catalysts and phenol. Namely, if the 2-oxazolidinone residue in the polymers and phenol formed a 1 : 1 complex, the following equation could be effective:

$$[\text{Phenol}]=[\text{OX}]_{\text{eff}}\,[\text{Phenol}]/[\text{Complex}]-K_{\text{d}}. \quad (1)$$

Here, [Phenol] and [Complex] are the equilibrium concentrations of phenol and the 1 : 1 complex between the 2-oxazolidinone residue and phenol, respectively. K_{d} is the equilibrium constant for the dissociation of the complex between the 2-oxazolidinone residue in the polymers and phenol. $[\text{OX}]_{\text{eff}}$ is the effective concentration of the 2-oxazolidinone residue in the polymers, which is accessible to phenol. Thus, the values of K_{d} and $[\text{OX}]_{\text{eff}}$ were determined from the intercepts and the slopes, respectively, for the straight lines in the plots of [Phenol] vs. [Phenol]/[Complex].

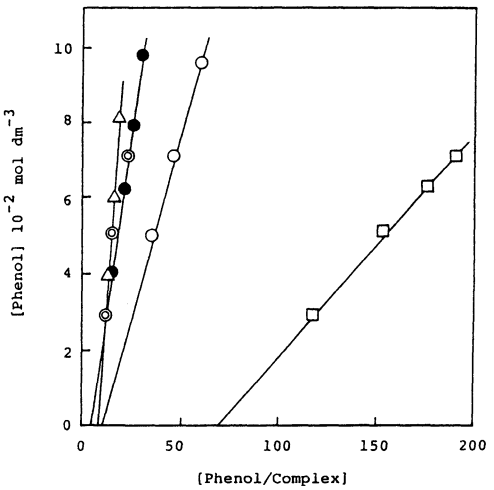


Fig. 1. Plots of [Phenol] vs. [Phenol]/[Complex] according to Eq. 1. △, data for POPA; ○, data for POS 1; ◎, data for POS 2; ●, data for POS 3; □, data for PHS.

Table 2. Complex Formation between the Polymer-Bound 2-Oxazolidinones and Phenol[a]

Substrate	K_{d} 10^{-2} mol dm^{-3}	Concentration of 2-oxazolidinone residue/10^{-3} mol dm^{-3}	
		$[\text{OX}]_{\text{eff}}$	$[\text{OX}]_{\text{charged}}$
PHS	3.83	0.564[b]	33.3[b]
POS 1	1.62	3.79	13.0
POS 2	1.60	3.77	11.9
POS 3	2.12	1.90	7.71
POPA	8.27	8.61	15.2

a) Reacted at 30 °C by using 200 mg of substrate. b) Showed as an amount of repeating unit in poly(4-hydroxystyrene).

The plots of [Phenol] vs. [Phenol]/[Complex] according to Eq. 1 for the polymers anchoring 2-oxazolidinone are shown in Fig. 1. As can be seen from this figure, a definitely linear correlation between [Phenol] and [Phenol]/[Complex] was observed for all the samples. These facts indicate that the 2-oxazolidinones generate a 1 : 1 complex with phenol.

The values of K_{d} and $[\text{OX}]_{\text{eff}}$ evaluated from the

plots in Fig. 1 are summarized in Table 2. It appears that the amount of complex generated between PHS and phenol is sufficiently low to be neglected. The $[OX]_{eff}$ value for POPA containing the OMB moiety indicates that about 57% of 2-oxazolidinone residues in the polymer generated the complex with phenol, while in the case of POS-polymers the amount of reacted phenol increased with an increase in the content of the 2-oxazolidinone residue in the polymers; however, only 20—30% of the polymer-bond 2-oxazolidinones were effectively complexed with phenol. Moreover, the K_d values for POS-polymers decreased with an increase in the content of the 2-oxazolidinone moieties. The variations of the K_d value and the low efficiency for the POS-polymers might be explained as follows: since, as previously described, the 2-oxazolidinone and phenol residues coexist in the POS-poymers, they interact with each other through inter- and intramolecular hydrogen bonding between carbonyl group in 2-oxazolidinone ring and phenolic hydrogen in the polymers; the number of free 2-oxazolidinone moieties decreases pronouncedly, and further complex formation between the previously coordinated 2-oxazolidinone moiety and fresh phenol becomes more difficult; i.e., this difficulty increases with an increase in the number of phenolic hydroxyl groups in the POS-polymer molecule. This explanation also supports the fact that 3-phenycarbamoyl-2-oxazolidinone gave only a small amount of the complex with phenol,[2] because of the intramolecular hydrogen bonding (Fig. 2). On the other hand, the reaction of POPA with phenol gave the highest K_d values of the series. POPA swells in organic solvents, but shrinks in water. The shrinkage of the polymer molecules prevents any effective segregation of the 2-oxazolidinone residues, and enhances the steric repulsion between two bulky phenolic substituents. This logical analysis allows us to conclude that K_d for POPA reaches large values. These results also suggest that the stability of the complexes is associated with the environmental conditions in the vicinity of the 2-oxazolidinone residue, rather than the 2-oxazolidinone content in the polymers.

As described above, the complex formation between polymer-bound 2-oxazolidinone and phenol has been reported only concerning *N*-substituted derivatives, such as polymer **1**. The polymer-phenol complexes were formed through hydrogen bonding between the carbonyl group in the 2-oxazolidinone ring and phenolic hydrogen. In these cases, 41—67% of the polymer-bound 2-oxazolidinones were effectively interacting with phenol.[6,12] However, since the reaction of 3-phenylcarbamoyl-2-oxazolidinone with phenol yielded only a small amount of the complex,[2] and no complex was formed by treating 3,5-diphenyl-2-oxazolidinone with phenol, 3-substituted 2-oxazolidinones are not, necessarily, effective ligands for phenol. On the other hand, the polymer-bound 2-oxazolidinone in this work has a hydrogen on a nitrogen atom adjacent to a carbonyl group in the 2-oxazolidinone ring. In this case, there is a possibility of forming an intramolecular hydrogen bonding between phenolic hydrogen and both N-H and C=O groups in the 2-oxazolidinone ring, as shown in Fig. 3. The IR spectra of the original OMB and the OMB-phenol complex are shown in Fig. 4. Several characteristic shifts observed near 3300 cm^{-1} and in the region 1800—1200 cm^{-1} support the idea that the complex was, indeed, formed through hydrogen bonding (Fig. 3).

Complex Formation of the Polymer-Bound 2-Oxazolidinone with Mercury(II) Acetate. When methanol was used as a solvent for mixing mercury(II) acetate and 2-oxazolidinone, a white precipitate was obtained. The mercury content (48.6%) for the precipitate suggests that one mercury atom formed a 1:2 complex with two moelcules of 2-oxazolidinone (see Table 3). The IR spectra of the starting 2-oxazolidinone and complex are shown in Fig. 5. The

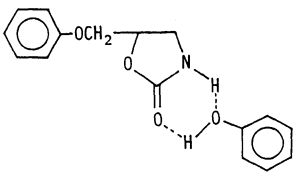


Fig. 3. Structure of the complex between PMO and phenol.

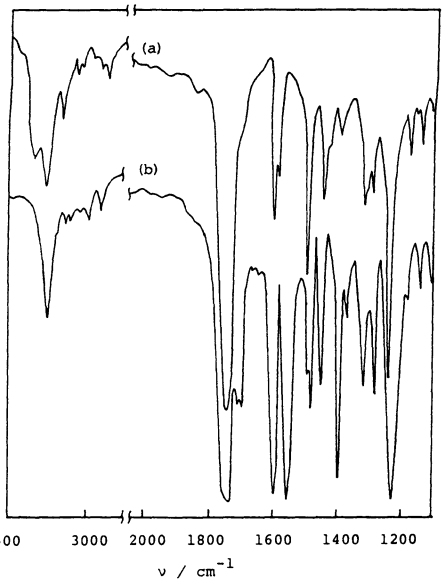


Fig. 4. IR spectra of PMO (chart a) and the complex between PMO and phenol (chart b).

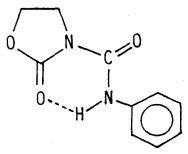


Fig. 2. Intramolecular hydrogen bonding in 3-carbamoyl-2-oxazolidinone.

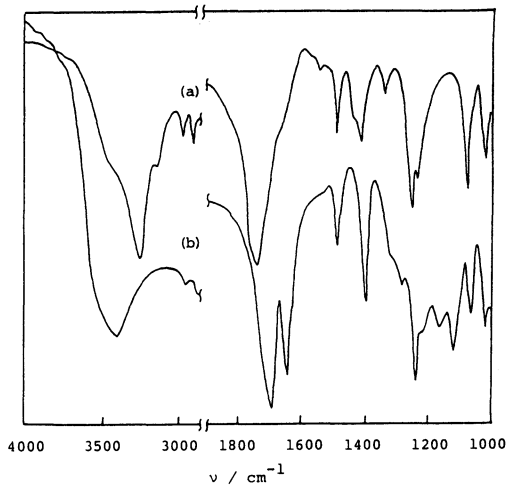


Fig. 5. IR spectra of 2-oxazolidinone (chart a) and the complex obtained from 2-oxazolidinone and mercury(II) acetate (chart b).

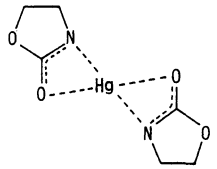


Fig. 6. Structure of the complex obtained from 2-oxazolidinone and mercury(II) acetate.

1740 cm^{-1} absorption band corresponds to the carbonyl stretching of 2-oxazolidinone shifted to 1705 cm^{-1} for the complex. In the case of the complex, furthermore, the 3280 cm^{-1} (N-H of 2-oxazolidinone) absorption band for the 2-oxazolidinone disappeared, and new absorption bands appeared at 1660 cm^{-1} and in the region 1200—1100 cm^{-1}. These two bands correspond to the C=N and C-O stretching vibration in the enol-type form of 2-oxazolidinone, respectively. Endo and co-workers[10] have reported on the formation of a 2:1 complex between 2-oxazolidinone and tin(II) chloride, with shifts of the IR absorption bands similar to those for the complex mentioned in this work.

In an ^1H NMR analysis, the chemical shifts of the pertinent protons in 2-oxazolidinone were observed at δ=3.45(t), 4.31(t), and 7.47(s). These signals have been assigned to the protons (H_a) attached to the ring carbon linked to nitrogen, to the protons (H_b) on a carbon atom attached to ring oxygen, and to the proton on the nitrogen atom, respectively.[20] However, the chemical shifts of the pertinent protons in the complex were observed at δ=3.60(t), and 4.30(t). The shift of the signal assigned to protons H_a and the disappearance of the signal assigned to proton on the nitrogen atom suggest that there is a considerable interaction between the mercury atom and the nitrogen atom adjacent to the protons H_a. Since no signal assigned to the pertinent protons in mercury(II) acetate was observed in the ^1H NMR spectrum of the complex, it is evident that the complex does not contain acetate ions.

Table 3. Complex Formation between the Polymer-Bound 2-Oxazolidinones and Mercury(II) Acetate[a]

Substrate	Amount of charged 2-oxazolidinone residue	Amount of mercury forming the complex	
	mmol	mmol[b]	mmol[c]
POS 1	0.328	0.007	0.164
POPA	0.381	0.160	0.191
OPA-St	0.359	0.079	0.180
OMB	0.262	0.095	0.131
2-Oxazolidinone	0.500[d]	0.226	0.250

a) Reacted at room temp in 10 cm^{-3} of 0.08 mol dm^{-3} mercury(II) acetate aq. solution. b) Determined by the change of absorbance in atomic absorption analysis. c) Calculated on the basis of assumption that the 2-oxazolidinone residue in the polymers and mercury atom formed a 2:1 complex. d) Reacted in methanol.

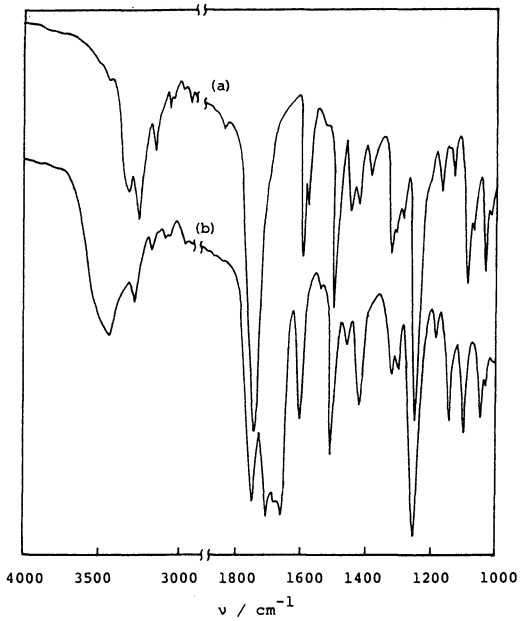


Fig. 7. IR spectra of PMO (chart a) and the complex obtained from PMO and mercury(II) acetate (chart b).

From these results, the reaction of 2-oxazolidinone (OxH) with mercury(II) acetate may be expressed in the form of Eq. 2; it seems reasonable to imagine that the structure of the resulting mercury compound is represented by the formula shown in Fig. 6.

$$2\,OxH + Hg(CH_3COO)_2 \rightarrow Hg(Ox)_2 + 2\,CH_3COOH \quad (2)$$

However, no precipitate was observed in the solution upon treating 2-oxazolidinone with several metal salts, which was tested by other means than mercury(II) acetate in this work. Spectrophotometrical evidence for the complex formation was not obtained.

On the other hand, OMB, POS 1, POPA, and OPA-St were treated with mercury(II) acetate under heterogeneous conditions in water, respectively. The results are listed in Table 3. The mercury content for the

OMB complex was only about 70% of the expected amount on the basis of an assumption that the polymer-bound 2-oxazolidinone and mercury atom formed a 2:1 complex. The IR spectra of the original OMB and OMB complex are shown in Fig. 7. As can be seen from the figure, the variations of absorption in both the 3500—3200 and 1740—1660 cm^{-1} regions indicate that the product obtained from OMB and mercury(II) acetate is a mixture of the original OMB and OMB complex, in comparison with Fig. 4. This is believed to be due to the formation of a complex on the solid surface of OMB.

The mercury content for the POPA complex reaches the highest value of the series, except for 2-oxazolidinone, and POPA absorbed about 80% of the amount originally expected. However, the mercury content was larger than that estimated on the basis of the $[OX]_{eff}$ value for complex formation between POPA and phenol. This result suggests that all the mercury atoms absorbed do not necessarily form a 2:1 complex, as shown in Fig. 6. It is thought that a mercury atom that chemically binds one mole of 2-oxazolidinone residue or/and is physically absorbed into polymer networks is present in the POPA-mercury complex. However, in the case of the polymer-mercury complexes, the IR-shifts were not so clearly observed. POS 1 and OPA-St, in spite of 58 and 85 mol% 2-oxazolidinone content, respectively, were not as absorptively effective as we had expected. The mercury contents for the polymers are in the order POPA->OPA-St->POS-complex; this order agrees with the 2-oxazolidinone content in the polymers. As can be seen in Table 3, a slight decrease in the 2-oxazolidinone content in the polymers affects the complex formation in a striking manner. The large discrepancies between the values calculated and determined for POS 1 and OPA-St can be explained on the basis of the assumption that, even if the polymers were used, two 2-oxazolidinone moieties in the polymers are consumed for binding one mercury atom. Since two 2-oxazolidinone moieties in the polymer are very far apart (as a function of the decrease in the 2-oxazolidinone content), their mutual cooperation in forming a 2:1 complex is effectively nil. In the case of POPA, therefore, the presumed 1:1 complex between the mercury atom and the 2-oxazolidinone residue may be neglected. As described above, POPA is insoluble and swelling in organic solvents and appears to be composed of networks of cross-linked polymers. Mercury(II) acetate which has permeated into the cross-linked POPA would be very difficult to remove, even by repeated washing with water, in comparison with soluble POS 1 and OPA-St.

It is, finally, concluded that one mercury atom forms a 1:2 complex with two molecules of 2-oxazolidinone. This relation concerning the molar ratio must apply to all forms of complexes between the mercury atom and the 2-oxazolidinone residue in polymers.

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