Synthesis of Polymers Containing the Pendant Oxazolidone Moiety and Their Complex-Forming Behavior with Phenols

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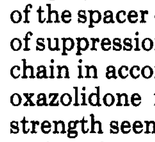
ABSTRACT: The synthesis and complex-forming behavior of a number of oxazolidone-containing cross-linked polystyrenes were investigated. Three oxazolidone-containing polymers with different spacer lengths between their main chains and the oxazolidone groups, NOES, NOHS, and NODS, were synthesized by the reaction of cross-linked poly(styrene-*co*-4-(chloromethyl)styrene) with 3-(2-hydroxyethyl)-, 3-(6-hydroxyhexyl)-, and 3-(12-hydroxydodecyl)oxazolidones, respectively. The complex-forming behavior of these polymers with phenols was studied in terms of the effect of the length of the spacers. The strength of the complex-forming capacity was evaluated as the binding constant (K), which was obtained by Klotz plots. K values obtained in water were larger than those in chloroform in any polymer. The K value in water increased with an increase of the methylene chain length of the spacer, whereas K values in chloroform were nearly equal in the polymers having methylene chain length $n \geq 6$. K values for the systems of these polymers and four phenols in chloroform depended on the acidity of the phenols. A good linear relationship between log K and the pK_a of the phenols indicated that the interaction is strengthened in proportion to lowering the pK_a of a phenol used. K values for the polymers having the oxazolidone moiety were compared with those for the polymers having the pyrrolidone moiety. A similar tendency was observed for the effect of methylene chain length and the difference in complex-forming behavior between water and chloroform. The relationship between log K and the pK_a of phenols was also the same. However, the degree of strength of the complex-forming capacity in the oxazolidone polymers was smaller than that of the pyrrolidone polymers. This result was also discussed.

Introduction

Synthetic polymers having cyclic amides or urethanes such as poly(vinylpyrrolidone) or poly(vinyloxazolidone) form fairly stable complexes with small molecules such as phenols, carboxylic acids, alkyl halides, and metals.[1-7] It has been suggested that these polymers interact with small molecules through various interactions such as hydrogen bonding, hydrophobic interaction, charge-transfer stacking, electrostatic interaction, and van der Waals forces. We have studied the interaction between phenols and bifunctional pyrrolidones as model compounds of poly(cyclic amides).[8] On the basis of the results of the model study, we have synthesized novel polymers (**I, II**)with a spacer between the main chain and the pyrrolidone moiety and investigated the adsorption–desorption of phenols on the polymers.[9,10] These results indicated that indroduction of the spacer enhances the adsorption of phenols, because of suppression of the steric hindrance of the polymer main chain in accordance with the model study. Although the oxazolidone moiety can also interact with phenols, its strength seems to be smaller than that of the pyrrolidone moiety from the results of the radical copolymerization behavior of vinyl monomers carrying such a moiety with *m*-vinylphenol.[11] It is interesting to investigate the effect of spacer length in the oxazolidone system and compare it with that of the pyrrolidone system. The present paper deals with the synthesis of polymers [**III**: NOES (n = 2), NOHS (n = 6), and NODS (n = 12)] having a pendant oxazolidone moiety with a spacer, their complex-forming behavior with phenols, and comparison of it with that of the polymers having a pyrrolidone moiety.



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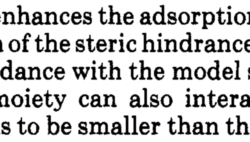

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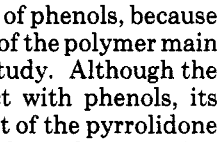

III

Experimental Section

Materials. Cross-linked poly(styrene-*co*-4-(chloromethyl)-styrene) was donated from Mitsubishi Kasei Corp. (Cl content 20.15 wt %, (chloromethyl)styrene unit 5.68 mmol/g). Solvents and reagents (2-bromoethanol, 6-bromohexanol, 12-bromododecanol, 2-pyrrolidone, phenol, 2-naphthol, 1,2-dihydroxybenzene, 2,3-dihydroxynaphthalene) were dried and distilled or recrystallized according to the usual manners. Other chemicals of reagent grade were used without further purification.

Synthesis of 3-(ω-Hydroxyalkyl)pyrrolidones. 3-(2-Hydroxyethyl)oxazolidone. The title compound was prepared according to the method of our previous paper.[11]

3-(6-Hydroxyhexyl)oxazolidone. The title compound was synthesized according to the procedure of 3-(2-hydroxyethyl)-oxazolidone with some modification. To a suspension of sodium hydride (55 wt % mineral oil dispersion, 5.21 g, 0.13 mol) in 200 mL of dry dimethylformamide (DMF) was added dropwise 2-oxazolidone (9.58 g, 0.11 mol) dissolved in 50 mL of dry DMF with stirring at room temperature. The mixture was kept at room temperature for 5 h. 6-Bromohexyl 2-pyranyl ether (29.1 g, 0.11 mol)[12] was dissolved in 50 mL of dry DMF, and the solution was added dropwise to the mixture with stirring at room temperature. The resulting mixture was heated at 60 °C for 5 h. After DMF was removed by distillation under a reduced pressure, the residue was extracted with ether and the organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was treated with a small amount of *p*-toluenesulfonic acid in 200 mL of methanol. The mixture was stirred at methanol refluxing temperature for 2 h. Methanol was evaporated, and the residual product was subjected to column chromatography on silica gel using ethyl acetate as eluent. Yield: 17.5 g (85%, yellow viscous oil). IR (neat): 3400 (OH), 2936 (CH_2), 2866 (CH_2), 1731 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$):

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δ 4.36–4.29 (t, J = 8.2 Hz, 2H, —CO—O—CH_2—), 3.68–3.61 (t, J = 6.5 Hz, 2H, HO—CH_2—), 3.61–3.50 (t, J = 8.2 Hz, 2H, —CO—O—CH_2—CH_2—), 3.26–3.22 (t, J = 7.1 Hz, 2H, —N—CH_2—), 1.69–1.42 (m, 8H, —CH_2— × 4) ppm. Anal. Calcd for $C_9H_{17}NO_3$: C, 57.75; H, 9.09; N, 7.49. Found: C, 57.30; H, 9.22; N, 7.05.

3-(12-Hydroxydodecyl)oxazolidone. The title compound was prepared by the same procedure as 3-(6-hydroxyhexyl)-oxazolidone. Yield: 22.7 g, (76%, white solid). Mp: 50–51 °C. IR (KBr): 3398 (OH), 2928 (CH_2), 2858 (CH_2), 1734 (C—O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 4.38–4.30 (t, J = 8.2 Hz, 2H, —CO—O—CH_2—), 3.69–3.61 (t, J = 6.5 Hz, 2H, HO—CH_2—), 3.61–3.52 (t, J = 8.2 Hz, 2H, —CO—O—CH_2—CH_2), 3.28–3.21 (t, J = 7.1 Hz, 2H, —N—CH_2—), 1.72–1.43 (m, 21H, HO—, —CH_2— × 10) ppm. Anal. Calcd for $C_{15}H_{29}NO_3$: C, 66.42; H, 10.70; N, 5.17. Found: C, 66.45; H, 10.32; N, 5.13.

Synthesis of Cross-Linked Polymers Having the Oxazolidone Moiety. Typical Procedure for NOES. To a suspension of sodium hydride (55 wt % mineral oil dispersion, 4.01 g, 0.10 mol) in 100 mL of dry DMF was added dropwise 3-(2-hydroxyethyl)oxazolidone (11.3 g, 0.086 mol) in 50 mL of dry DMF with stirring at room temperature. The mixture was stirred at room temperature for 5 h. Cross-linked poly(styrene-*co*-4-(Chloromethyl)styrene) (12.5 g, 0.072 mol) was added to the mixture with stirring at room temperature. The resulting mixture was stirred at 60 °C for 5 h. Solvent-insoluble material was collected by filtration and extracted by Soxhlet extractor with methanol and *n*-hexane. The obtained polymer was dried under reduced pressure and sieved in grain size ranging from 0.17 to 0.43 mm. IR (KBr): 2922 (CH_2), 2856 (CH_2), 1747 (C—O), 1096 (—O—) cm^{-1}. Anal. N content: 3.68 (4-[[2-(2-oxo-3-oxazolidinyl)ethoxy]methyl]styrene unit: 2.67 mmol/g).

By similar procedures, NOHS and NODS were obtained.

NOHS. IR (KBr): 2923 (CH_2), 2856 (CH_2), 1740 (C=O), 1114 (—O—) cm^{-1}. Anal. N content: 3.03 (4-[[6-(2-oxo-3-oxazolidinyl)hexanoxy]methyl]styrene unit: 2.17 mmol/g).

NODS. IR (KBr): 2924 (CH_2), 2854 (CH_2), 1743 (C=O), 1113 (—O—) cm^{-1}. Anal. N content: 2.67 (4-[[12-(2-oxo-3-oxazolidinyl)dodecanoxy]methyl]styrene unit: 1.91 mmol/g).

General Procedure for Complex Formation Between Polymers and Phenols. An oxazolidone moiety-containing cross-linked polymer (100 mg) was added to a 10 mL water or chloroform solution of a phenol (concentration ranging from 0.02 to 0.2 mol/L). The heterogeneous mixture was shaken by a shaker at 22 °C for 5 h. The polymer was removed by filtration, and the concentration of the phenol remaining in the filtrate was measured by UV (absorption at 270 (phenol), 275 (2-naphthol), 277 (1,2-dihydroxybenzene), and 283 nm (2,3-dihydroxynaphthalene)).

Measurement. ^{1}H-NMR spectra were recorded on a Bruker AC-P300 (300 MHz) using tetramethylsilane as an internal standard. FT-IR spectra were obtained with a JASCO FT/IR-5000 spectrophotometer. UV spectra were measured with a Hitachi U-3200 spectrophotometer.

Results and Discussion

Preparation of Polymers Having the Oxazolidone Moiety. Cross-linked polymers (NOES, NOHS, and NODS) with a spacer between the polymer main chain and the oxazolidone moiety were prepared by the reaction of cross-linked poly(styrene-*co*-4-(chloromethyl)styrene) with 3-(ω-hydroxyalkyl)oxazolidone, as shown in Scheme 1. The obtained polymers were sieved in grain size ranging from 0.17 to 0.43 mm. As shown in Figure 1b, the IR spectrum of NOES shows two characteristic absorption bands at 1730 (C=O of 2-oxazolidone) and 1100 cm^{-1} (C—O of the ether structure). The oxazolidone content in the polymers was determined by the N content obtained from elemental analysis and was 2.67 (for NOES), 2.17 (for NOHS), or 1.91 mmol/g (for NODS). The degree of etherification of the chloromethyl group ranged from 40 to 60%, which was not too high, probably because of the bulkiness of the oxazolidone terminal alkoxy groups.

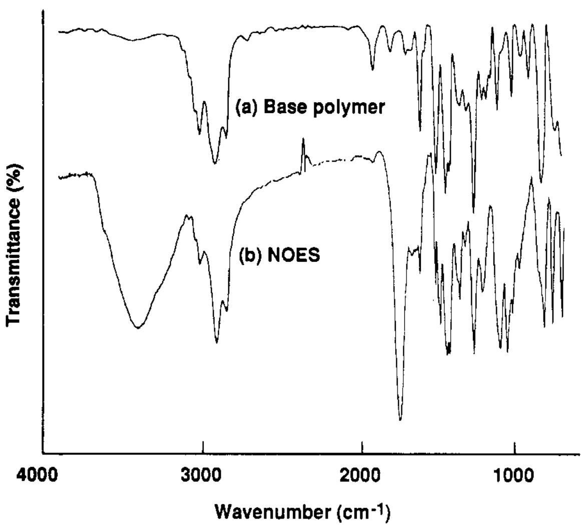
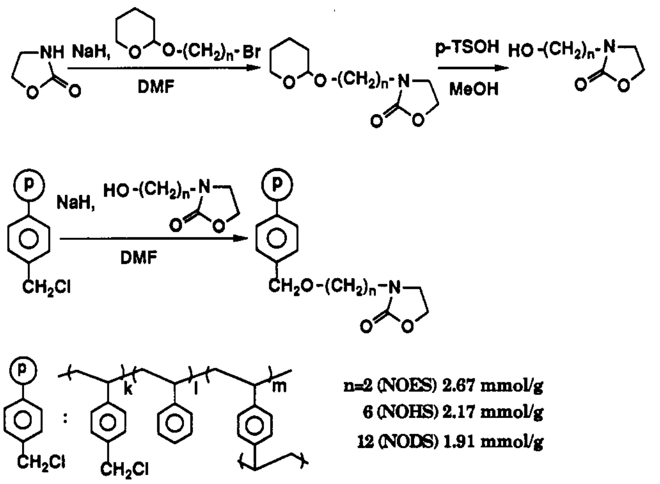


Figure 1. IR spectra (KBr) of base polymer (a) and NOES (b).

Scheme 1



Complex-Forming Behavior of the Polymers with Phenols. The oxazolidone-containing polymers were added to a solution of a phenol in water or chloroform, and the heterogeneous mixture was shaken at 22 °C for 5 h. The concentration of phenols which were not adsorbed in the polymers was measured by UV. In these systems, it took *ca.* 5 h to attain a complete adsorption equilibrium in any case. To evaluate the extent of the interaction between the polymers and phenols, the Klotz equation[13] (eq 1)was used. Here, K is the binding constant, r is the

$$\frac{1}{r} = \frac{1}{nKa} + \frac{1}{n} \qquad (1)$$

number of moles of the phenols bound per-1 mol of the oxazolidone unit in the polymers, n is the number of binding sites per one oxazolidone unit (site-density value), and a is the molar concentration of free phenols at an equilibrium.

Figures 2 and 3 show plots of $1/r$ *vs* $1/a$ for the systems between the polymers and phenol in water and 2-naphthol in chloroform, respectively, according to eq 1. Here, the slope is $1/nK$ and the intercept is $1/n$. Good linear relationships between $1/r$ and $1/a$ were found in both systems. In the other systems between the polymers and phenols similar good linear relationships were also confirmed. The binding constants (K) and the site-density values (n) obtained from the Klotz plots are listed in Table 1.

Table 1. Binding Constant (*K*) and Site Density (*n*) between Polymers Having the Oxazolidone Moiety and Phenols in Water or Chloroform at 22 °C

polymer	methylene chain length	phenols	solvent	*K* (mol/L)	1/*n*	pK_a[a]
NOES	2	phenol	water	24.2	0.61	9.98[b]
NOHS	6	phenol	water	27.4	0.47	
NODS	12	phenol	water	30.6	0.41	
NOES	2	phenol	chloroform	15.2	1.44	
NOHS	6	phenol	chloroform	20.3	0.88	
NODS	12	phenol	chloroform	20.9	0.92	
NOES	2	2-naphthol	chloroform	17.0	1.37	9.93[c]
NOHS	6	2-naphthol	chloroform	26.6	1.08	
NODS	12	2-naphthol	chloroform	25.2	0.85	
NOES	2	1,2-dihydroxybenzene	water	53.6	0.67	9.13[c]
NOHS	6	1,2-dihydroxybenzene	water	67.6	0.62	
NODS	12	1,2-dihydroxybenzene	water	78.8	0.58	
NOES	2	1,2-dihydroxybenzene	chloroform	29.2	1.26	
NOHS	6	1,2-dihydroxybenzene	chloroform	63.4	0.97	
NODS	12	1,2-dihydroxybenzene	chloroform	64.9	1.30	
NOES	2	2,3-dihydroxynaphthalene	chloroform	65.1	1.11	8.68[d]
NOHS	6	2,3-dihydroxynaphthalene	chloroform	164	1.30	
NODS	12	2,3-dihydroxynaphthalene	chloroform	148	0.84	

[a] In aqueous solution at 25 °C. [b] Reference 15. [c] Reference 16. [d] Reference 17.

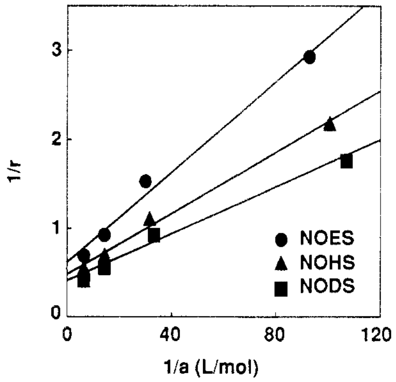


Figure 2. Klotz plots of 1/*r* *vs* 1/*a* for the systems of the polymers having the oxazolidone moiety and phenol in water at 22 °C.

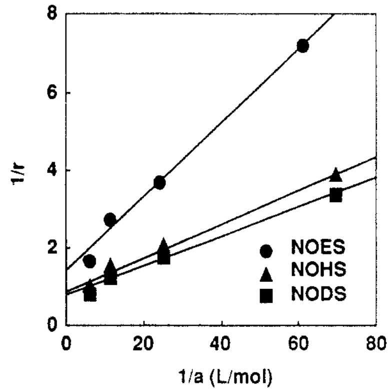


Figure 3. Klotz plots of 1/*r* *vs* 1/*a* for the systems of the polymers having the oxazolidone moiety with 2-naphthol in chloroform at 22 °C.

From the Klotz plots 1/*n* for phenol and 1,2-dihydroxybenzene was evaluated to be *ca.* 0.5 (0.41–0.67), while in chloroform 1/*n* was *ca.* 1 (0.88–1.44). The site-density value (*n*) in water was about 2 times larger than that in chloroform. As for other phenols 1/*n* in chloroform was similarly *ca.* 1 (0.84–1.37). In the case of pyrrolidone polymers having structures similar to the oxazolidone polymers, *n* values for phenols were *ca.* 2 in water and *ca.* 1 in chloroform[14] in accordance with the above systems.[10] The clear solvent dependency of *n* values would be accounted for by assuming a hydrophobic interaction, an extra interaction which can be seen in water but not in chloroform, as described in the following discussion on the binding constant (*K*). Namely, the site-density value being larger in water than in chloroform is attributed mainly to the adsorption of phenols on the basis of the hydrophobic interaction with the polymers in water.

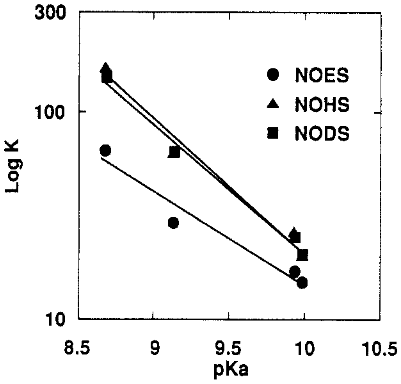
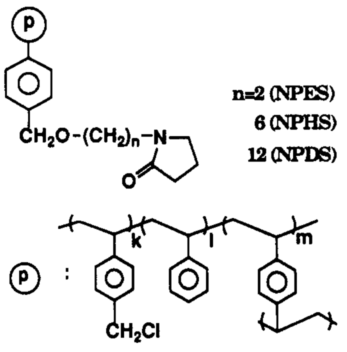


Figure 4. Plots of log *K* *vs* pK_a of the phenols (data in chloroform in Table 1).

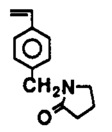
K values observed in water for the system with phenol and 1,2-dihydroxybenzene were larger than those in chloroform for any polymer, probably because the interaction in chloroform was caused mainly by hydrogen bonding while the interaction in water was attributed not only to hydrogen bonding but also to hydrophobic interaction. The *K* value in water increased with an increase of the methylene chain length of the spacer in the polymers. Namely, the polymer with the longer methylene chain more effectively formed its complex with phenol and 1,2-dihydroxybenzene, compared with the polymer with the shorter one. This would be explained by the high complex-forming capacity facilitated by the prolonged alkyl chain spacer and/or by the enhanced hydrophobicity by the increase in the methylene chain length. On the other hand, in the case of the polymer with the number of methylenes $n \geq 6$, *K* values in chloroform were almost the same. This result suggests that the methylene chain length is long enough to effectively form the complex with phenol and to ignore the effect of the steric hindrance based on the polymer main chain. In the systems of the polymers with 2-naphthol, 1,2-dihydroxybenzene, and 2,3-dihydroxynaphthalene, a similar tendency was observed.

K values in chloroform decreased in the following order: 2,3-dihydroxynaphthalene > 1,2-dihydroxybenzene > 2-naphthol > phenol. The order can be explained by the acidity of these phenols, because *K* values increase with an increase of acidity of the phenols: a more acidic phenol interacts more strongly with the polymers. The plots of log K *vs* pK_a of the phenols, as shown in Figure 4, gave a good linear relationship with any polymer. This result, therefore, suggests that the major interaction in these systems should be hydrogen bonding.

In our previous paper,[9,10] we have reported the complex-forming behavior of pyrrolidone-containing polymers having similar structures (NPES, NPHS, and NPDS).



As for the effect of methylene chain length, two polymers, oxazolidone- and pyrrolidone-containing polymers, showed similar tendencies. Namely, the binding constant K value increased with an increase of the methylene chain length of the spacer in water, whereas in chloroform the polymers with the methylene chain length $n \geq 6$ had almost the same K values. In addition, a figure similar to that for the relationship between K and the pK_a of phenols was obtained. However, whole K values for the oxazolidone-containing polymers were smaller than those for the pyrrolidone-containing polymers in any case. For example, $K = 17.2$ for NPES, whereas $K = 15.2$ for NOES. This is of course well consistent with our expectation as described at first in this paper. The most probable reason for this difference should be the difference in strength of the interaction based on hydrogen bonding, judging from the pronounced importance of hydrogen bonding among all interaction forms. As another reason, charge transfer (CT) stacking is conceivable, although it would directly affect the K value much less than hydrogen bonding. In the oxazolidone polymer systems, both hydrogen bonding and hydrophobic interaction are suggested as major interactions for the complex formation in water, while in addition to the two interactions, CT stacking is also considered as one of the major interactions in the case of the pyrrolidone polymer systems. Consequently, it would be clarified that the difference in complex forming behavior between the two polymer systems results from the difference in the degree of interaction with phenols, especially in the strength of hydrogen bonding. A noteworthy problem may arise from a synergistic effect of hydrogen bonding and CT stacking in the case of the pyrrolidone-containing polymers. As mentioned in the previous paper concerned with the model study using bifunctional pyrrolidones,[8] both interactions can strengthen each other because electron donation from the phenol ring to the pyrrolidone ring by the CT interaction should enhance its hydrogen bonding capacity in the pyrrolidone polymer systems. If this is the case, the essential difference in capability of hydrogen bonding between these two kinds of polymers is rather smaller than that appearing in the K values. In our previous examination on the capacity of hydrogen bonding, the difference in low frequencies shift of the carbonyl absorption by addition of phenol derivatives between 4-[(1-pyrrolidonyl)methyl]styrene (PS) and 4-[(3-oxazolidonyl)methyl]styrene (OS) is large (19 cm^{-1}) when phenol is used but is zero when 4-*tert*-butylphenol is used. Namely, since CT stacking seems not to occur when 4-*tert*-butylphenol is used, it can be reasonably considered that the two polymers have similar hydrogen bonding capacities. At the present time, we can only conclude that as a result the pyrrolidone-containing polymers have a hydrogen bonding capacity larger than the oxazolidone-containing polymers.



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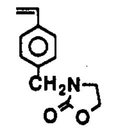

OS

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