# Twisted Polymers: Structural Reorganization in Macromolecular Network Through Metal Ion Coordination

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## Synopsis

The alkylation of flexible styrene–divinylbenzene copolymer, with 5-chloromethyl-8-hydroxy-quinoline in the "impregnated" dry state in the presence of aluminum chloride in nitrobenzene, is accompanied by structural reorganization. The polymer external shape is twisted and the internal structure constringes or expands, according to the impregnation method. The process of the "twist" polymer formation can be explained by the coordination of aluminum ions by the oxine ligand concurrently with the alkylation.

## INTRODUCTION

The structure of the macromolecular network of ion exchange resins has a fundamental role in directing ion exchange processes. Ion exchange kinetics and ion selectivity can be manipulated through modification of the network.[1,2]

The "primary" polymer network structure is determined by the monomer type, the nature of the crosslinking agent, and its concentration. The polymerization technique will then induce a macroreticular,[3] expanded,[4] or isoporous[5] network structure. "Secondary" modification of the network is usually introduced by crosslinking during subsequent chloromethylation reaction.

Working on the functionalization of styrene–divinylbenzene copolymers by Friedel–Crafts alkylation,[6] we have noticed the reaction to be strongly dependent on the metal-coordinating powers of the substituted benzyl halide. The most striking effects were obtained for the strongest ligating substrates.

Neckers et al.[8] have described the preparation of a tightly bound complex of aluminum chloride–polystyrene and some synthetic applications. The present work reports on the structural reorganization of the styrene–divinylbenzene network, caused by alkylation of the polymer with 5-chloromethyl-8-hydroxy-quinoline, in a dry "impregnated" state.

## RESULTS AND DISCUSSION

### Alkylation of XE-305 with 5-Chloromethyl-8-hydroxyquinoline Under Various Conditions

Earlier[6] we have established that XE-305, a 4% divinylbenzene–styrene co-polymer,[7] is very suitable for functionalization with large substrates, such as substituted aromatic compounds, since it swells very well in nitrobenzene.

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The alkylation of XE-305 with 5-chloromethyl-8-hydroxyquinoline (CHQ) in 1.8$M$ aluminum chloride (A) in nitrobenzene (N) is described below.
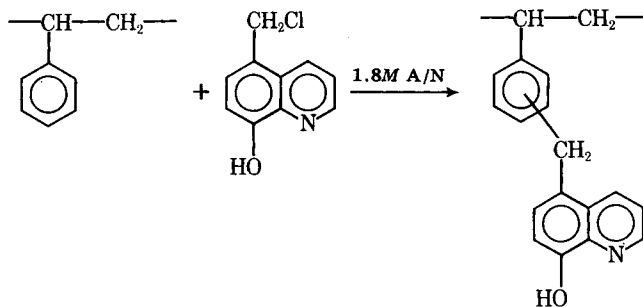


The reaction was performed under four sets of conditions:

1. The ordinary method.  All the reactants were mixed together.  Excess nitrobenzene solvent was used.

2. All the reactants were mixed together, but the volume of the A/N solution was precalculated to be exactly absorbed by the polymer.

3. The polymer was first impregnated by 5-chloromethyl-8-hydroxyquinoline from chloroform.  The solvent was then removed and the polymer immersed in a precalculated volume of A/N solution, which was totally absorbed by the polymer.

4. As in (3), but HCl gas was passed to convert the amine into the hydrochloride, and then immersed in a precalculated volume of A/N solution.

Although the alkylation yields are very similar for all the methods, (see Table I) the products differ by their shape.

Polymers 1 and 2 prepared by methods (1) and (2) have an ordinary, perfectly round shape, as shown in Figure 1 for polymer 2.  Products of the reactions by methods (3) and (4) are round-twisted polymers.  The product of method (3) has the highest developed shape with distinct features (Fig. 2), whereas the product of method (4) has a rougher appearance (Fig. 3).
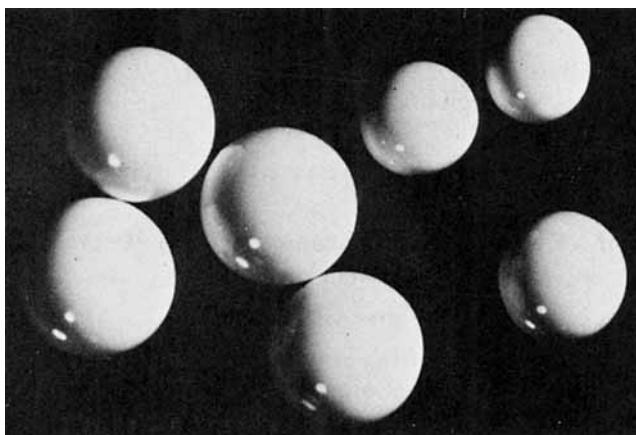


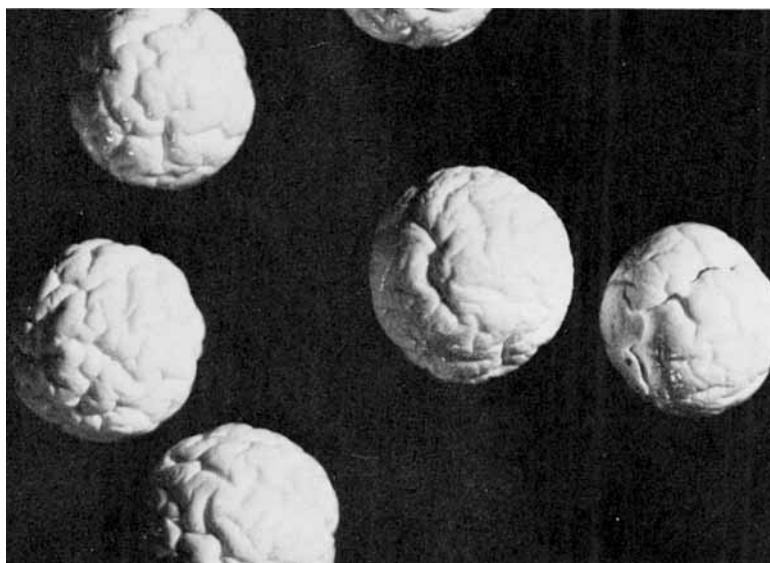Fig. 1. Round-shaped polymer 2, typical methods (1) and (2), prepared from XE-305 (×10).

Fig. 2. Round-twisted polymer 3, prepared by method (3) from XE-305 (×10).

## Alkylation of Other Polymers: Amberlite XAD-2 and XAD-4

In order to establish whether the round-twisted shape is particularly related to the alkylation method or whether it also relates to the polymer structure, we have conducted experiments on highly crosslinked polymers, Amberlites XAD-2 and XAD-4.

The products of the alkylation of XAD-2 and XAD-4 with 5-chloromethyl-8-hydroxyquinoline by method (4) (see Table I) are perfectly round-shaped beads (as shown in Fig. 4 for XAD-2).
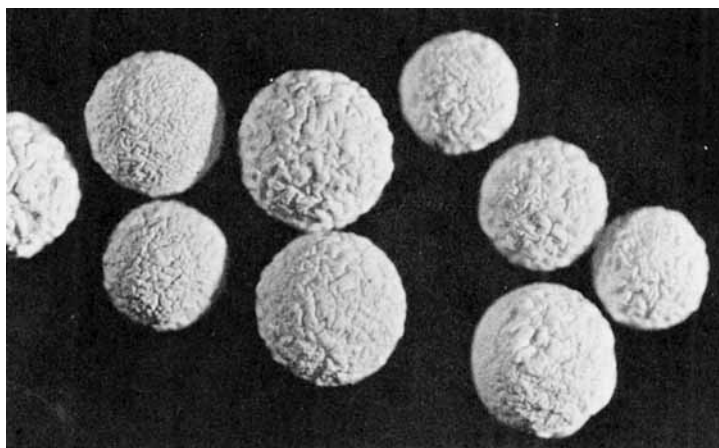


Fig. 3. Round-twisted polymer 4, prepared by method (4) from XE-305 (×10).

TABLE I

Alkylation of Various Styrene–Divinylbenzene[a] Copolymers with 5-Chloromethyl-8-hydroxyquinoline

| Polymer | Alkylation conditions | | | | | Incorporation in alkylated polymer[d] from | | | Shape | Figure No. |
|---|---|---|---|---|---|---|---|---|---|---|
| | CHQ,[b] mmoles | 1.8M AlCl₃ in nitrobenzene, ml | Temp., °C | Method[c] | No. | Weight increase | %N | %Cl | | |
| XE-305 | 8.7 | 15 | 70 | A | 1 | 1.03 | 1.08 | 0.87 | ordinary spherical | 1 |
| | 6 | 6 | 70 | B | 2 | 1.32 | 0.46 | 1.32 | ordinary spherical | 2, 6 - |
| | 6 | 6 | 70 | C | 3 | 1.82 | 1.28 | 2.36 | twisted | 3, 7, 8 |
| | 8.7 | 6 | 70 | D | 4 | 1.82 | 0.35 | 2.09 | twisted | |
| | 8.7 | 6 | R.T. | D | 5 | | 0.44 | | twisted | |
| | 8.7 | 6 | 150 | D | 6 | | 0.41 | | twisted | |
| XAD-2 | 8.7 | 5 | R.T. | D | 7 | 0.45 | 0.28 | | ordinary spherical | 4 |
| | 8.7 | 5 | 70 | D | 8 | 1.44 | 0.29 | | ordinary spherical | |
| XAD-4 | 8.7 | 5 | R.T. | D | 9 | 1.44 | 0.50 | | ordinary spherical | |

[a] Two g polymer, 72 hr.
[b] CHQ = 5-Chloromethyl-8-hydroxyquinoline.
[c] See experimental part.
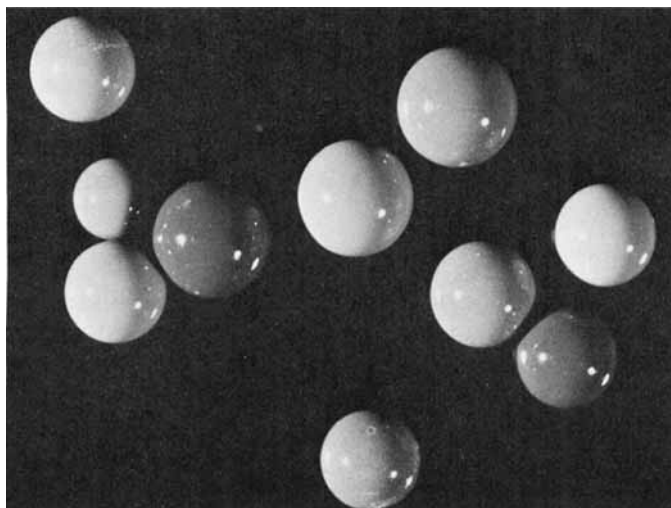[d] mmole methylene-hydroxyquinoline hydrochloride groups per gram polymer.

Fig. 4. Round-shaped polymer 8, prepared by method (4), from XAD-2 (same shape for XAD-4) (×10).

## Formation of Twisted XE-305 Polymers at Various Temperatures

The alkylation of XE-305 with 5-chloromethyl-8-hydroxyquinoline in the impregnated state was tried at various temperatures: room temperature (polymer 5), 70°C (polymer 4), and 150°C (polymer 6). The results were similar, the products having always the twisted shape. The fact that the twisted polymer is obtained throughout this temperature range, especially at the lowest temperature, rules out the possibility that other transformations are involved (for example, transformation at the glass transition temperature).
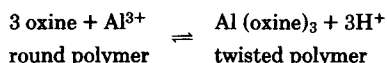
## Alkylation with Other Chloromethyl-Substituted Phenols by Method (3)

To check whether the twisted polymers are obtained by method (3) with 5-chloromethyl-8-hydroxyquinoline alone or with other metal-chelating ligands, we have attempted[6] the alkylation of XE-305 with 4-chloromethyl-2-nitrophenol and 4-chloromethyl-2-formylphenol, using alkylation method (3). In both cases the products had the ordinary perfect round shape.

## Alkylation of XE-305:  Role of the Impregnation Method

From the evidence collected so far, it is clear that the formation of the twisted polymer happens only with the highly flexible XE-305 and only if the alkylating agent forms very strong metal complexes, as is the case with 8-hydroxyquinoline (oxine). It was therefore interesting to establish at what stage of the procedure the polymer structural reorganization leading to the twisted shape occurs. Does this happen during the formation of the aluminum–5-chloromethyl-8-hydroxyquinoline complex or only during the subsequent covalent binding to the polymer? For that reason the model compound 8-hydroxyquinoline, which can form only an aluminum complex but not be covalently attached to the polymer, was studied.

8-Hydroxyquinoline was impregnated by method (3) and immersed in 1.8$M$ aluminum chloride in nitrobenzene.  Examination under the microscope revealed that the beads have acquired a distorted or even a twisted shape, similar to that in Figure 3.  However, when the beads were immersed in methanol to decompose the aluminum–oxinate complex and washed with chloroform, they returned to their original perfect round shape.  The reaction is described as follows:

$$3 \text{ oxine} + \text{Al}^{3+} \rightleftharpoons \text{Al (oxine)}_3 + 3\text{H}^+$$

$$\text{round polymer} \qquad \text{twisted polymer}$$

Since 8-hydroxyquinoline does not bind chemically to the polymer, this reaction is reversible, and the polymer emerges from this treatment with the original round-bead shape.

In the case of 5-chloromethyl-8-hydroxyquinoline, two reactions take place. First, fast complexation of the incoming aluminum chloride to form the stable octahedral hexadentate complex, followed by slow alkylation of the polymer, as described below (the blocked formulas relate to reagents and reactions in the impregnated state):



normal polymer

twisted polymer
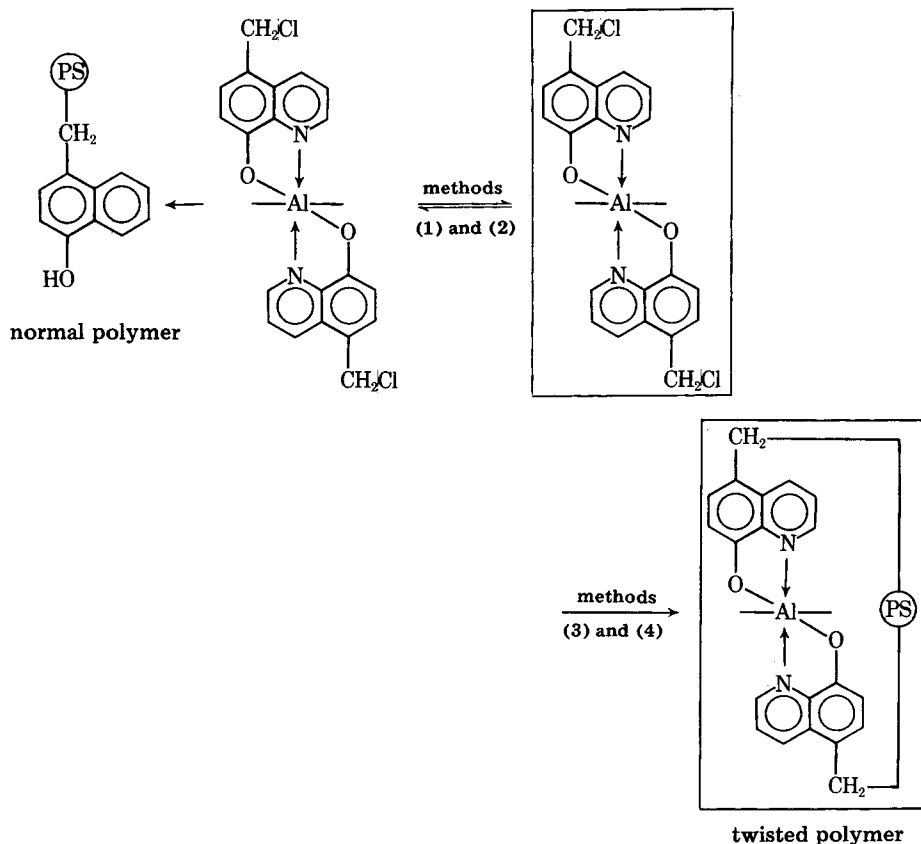
where PS stands for polystyrene.  In method (1), the tris(5-chloromethyl-8-hydroxyquinoline) aluminum complex is present in the polymer in low concentration, as it is free to diffuse into the bulk solution, and during the alkylation binds to the polymer with one of the three —CH$_2$Cl groups.  This covalent

binding results in a normal, round-bead polymer. In method (2), the diffusion of the aluminum–ligand complex into the polymer is very slow as the hydrophobic polymer resists swelling in the highly polar 1.8$M$ aluminum chloride solution (XE-305 swells fully in nitrobenzene within a few hours but does not swell in 1.8$M$ aluminum chloride/nitrobenzene solution after 9 days).

The alkylation of XE-305 under the conditions of method (2) proceeds therefore by a shell progressive mechanism, which is known for the related chlorosulphonation reaction.[8] By this mechanism the surface shell is first alkylated and is rendered polar. The aluminum chloride is then able to penetrate through this shell and further alkylate a second shell, and so on. This mechanism involves again low reagent and catalysts concentrations and does not lead to polymer structural rearrangements.

When XE-305 is alkylated in the impregnated state, methods (3) and (4), the high concentration of tris(5-chloromethyl-8-hydroxyquinoline) aluminum leads to covalent binding of this complex with two or three —$CH_2Cl$ groups. Since this is accomplished in a highly plasticized state when the polymer chains are free to move and undergo conformational changes, this leads to the structural rearrangement, resulting in the twisted polymers.

When the alkylation is performed on rigid polymers (XAD-2, XAD-4), it does not lead to twisted polymers, since the polymer chains are unable to undergo conformational changes.

## Scanning Electron Microscope (SEM) Examination

Scanning electron micrographs were taken of fractured beads obtained by immersion in liquid nitrogen. The SEM photograph of Amberlite XE-305 is shown in Figure 5. This is a typical SEM picture of a macroreticular styrene–divinylbenzene copolymer (×7200).
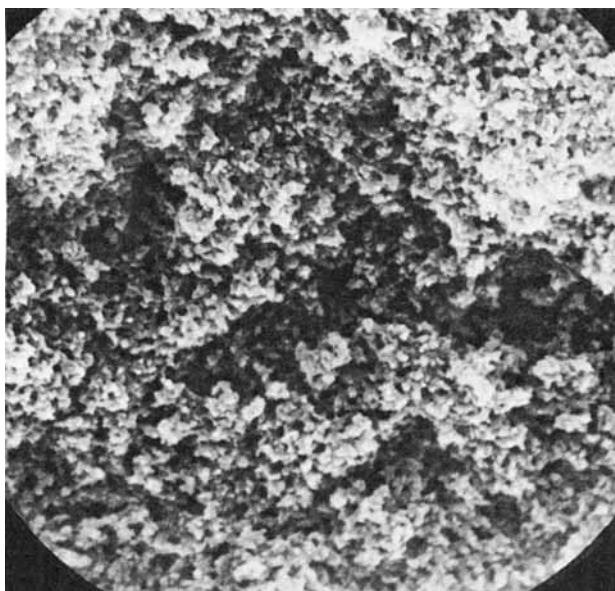


Fig. 5. Scanning electron microscope (SEM) picture of Amberlite XE-305 (×7220).

Fig. 6. SEM picture of the internal surface of fractured polymer 3 (×3000).

Figure 6 (×7220) shows the internal structure of a fractured bead of polymer 3, prepared by method (3). There is a striking constriction of the polymer structure, which resembles more a gel type. On the other hand, polymer 4, prepared by method (4), shows a significant change in the other direction, namely, expansion and formation of larger channels, as shown in Figure 7 (×3000). The reason for this difference is yet unclear.
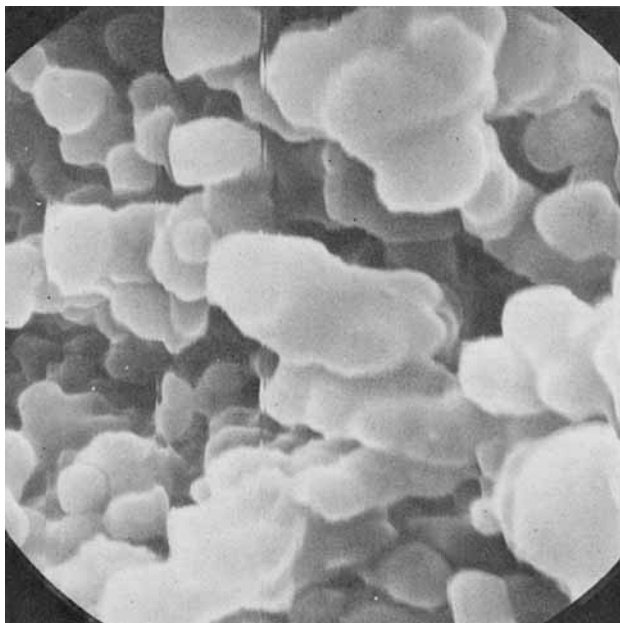

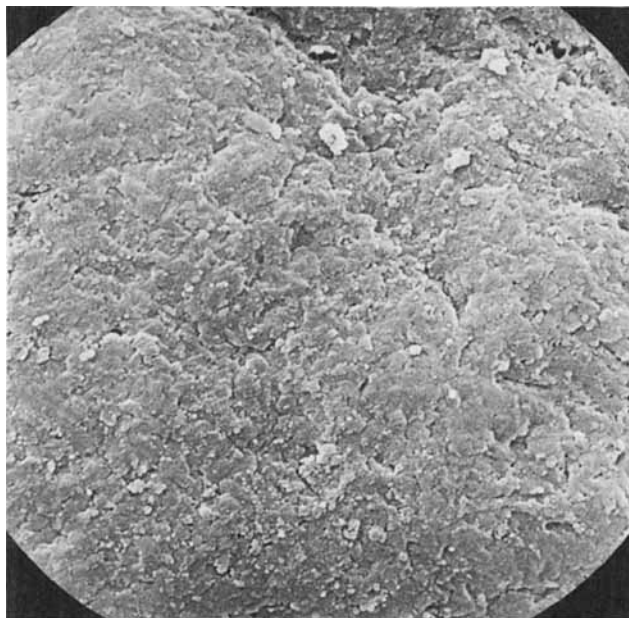
Fig. 7. SEM picture of the internal surface of polymer 4 (×7220).

Fig. 8. SEM picture of external surface of polymer 4 (×4820).

A close look at the external surface structure of polymer 4 is shown in Figure 8 (×4820), which suggests a very high surface indeed. Figure 9 (×7220) shows how the reversible twisting of XE-305 with 8-hydroxyquinoline has left a mark on the polymer external surface.
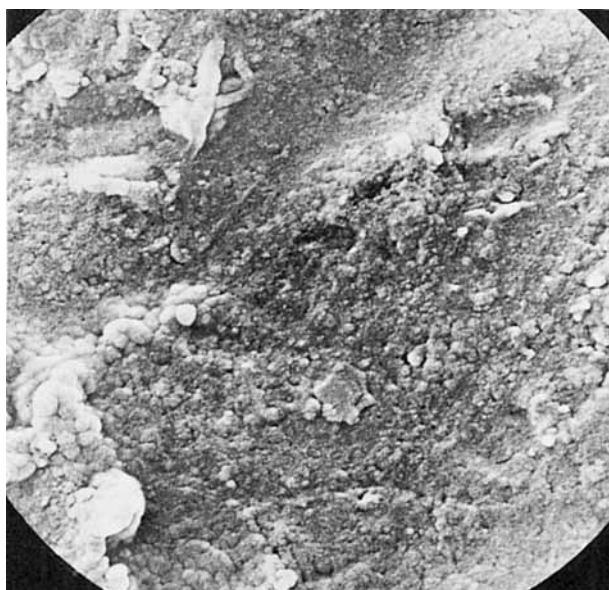


Fig. 9. SEM picture of external surface, 8-hydroxyquinoline reversible impregnation (×7220).

## Metal Coordination Properties

Table II describes the ion capacity for some of the oxine-type polymers, determined in $0.05M$ metal sulfate solution, pH = 2. The ordinary round-shaped polymers have an exchange capacity of 0.19–0.31 mmole $Cu^{2+}$ per gram polymer and of 0.2 mmole $Fe^{3+}$ per gram polymer (see Table II).

The capacity of polymers 3 [method (3)] and 5 [method (4)] are virtually zero. Examination of the analytical data (Table I) suggests that the high weight increase and high chlorine analysis (compared to the low nitrogen analysis) are due to the incorporation of $AlCl_3$. This explains very well the zero exchange capacity.

# CONCLUDING REMARKS

The experimental evidence presented shows that flexible polymers in a highly swollen state, and containing high concentration of metal–ligand complexes, are able to undergo structural rearrangements to comply with the steric requirements of the metal complex. This structural rearrangement is strongly dependent on the experimental conditions. In method (1), when excess free solvent is available, the aluminum–oxinate complex is free to diffuse out of the polymer and into the bulk solution.

In method (2), although excess solvent is not provided and the aluminum–oxinate is therefore not free to diffuse, the limiting factor is the slow diffusion of the aluminum chloride and nitrobenzene into the polymer.

In method (3), the availability of the ligand inside the polymer accelerates the diffusion of the catalyst. The fast formation of the complex, with a concurrent alkylation, is responsible for the macroreticular network rearrangement and production of the twisted polymer.

Method (4) is basically similar to method (3), except that the preliminary protonation of the oxine modifies somewhat the rate of the metal–ligand complex formation, resulting in a moderated twisted polymer.

The example of macromolecular network structure modification by metal coordination presented in this work can be probably extended to other strong metal–coordinating ligands and similarly to other flexible polymers. The interesting questions that remain to be explored are whether "structure printing in polymers" by metal coordination is possible or whether one is able to design and prepare polymers of the following properties: (1) chiral-twisted polymers; (2) ion-tailored polymers; (3) polymers incorporating "tailored holes." If this can be done, then "twisted polymers" will be more than a curiosity.

TABLE II
Metal-Complexing Experiments

| Polymer No. | Matrix | Preparative method | Ion capacity, mmole/g[a] | |
|---|---|---|---|---|
| | | | $Cu^{2+}$ | $Fe^3$ |
| 2 | XE-305 | (2) | 0.31 | 0.18 |
| 3 | XE-305 | (3) | 0.07 | 0.04 |
| 5 | XE-305 | (4) | 0.06 | <0.01 |
| 8 | XAD-2 | (4) | 0.19 | 0.06 |
| 9 | XAD-4 | (4) | 0.25 | 0.23 |

[a] Determined at $0.05M$ ion concentration.

## EXPERIMENTAL

### Materials

**Polymers.** Amberlites XE-305, XAD-2, and XAD-4 were obtained by courtesy of Rohm and Haas, U.S.A. The polymers were washed in HCl, H₂O, 1N NaOH, DMF, and methanol, then dried at 80°C for 24 hr. No nitrogen or chlorine could be detected in polymer samples after this washing procedure.

**Substituted Phenols.** 5-Chloromethyl-8-hydroxyquinoline hydrochloride,[6] mp 225°C decomp.; 8-hydroxyquinoline (A.R. grade) Fluka.

**1.8M Aluminum Chloride in Nitrobenzene (A/N Solution).** 24.3 g aluminum chloride from a freshly opened ampoule was dissolved in 100 ml nitrobenzene (A.R. grade) which was standing over calcium chloride in an Erlenmeyer fitted with a calcium chloride drying tube.

### Nitrobenzene Swelling Capacity of the Polymers

Two g of dry polymer sample was placed in 2 ml nitrobenzene for 24 hr. The solvent was completely absorbed on the polymer. Nitrobenzene was added in 5-ml portions until excess liquid was absorbed after an equilibration period of 48 hr. The swelling capacities are 5.5, 2.25, and 2.5 ml nitrobenzene per gram XE-305, XAD-2, and XAD-4, respectively.

### Swelling of XE-305 in 1.8M Aluminum Chloride in Nitrobenzene

Two g XE-305 was left in 2 ml 1.8M A/N solution for nine days. No swelling was observed.

### The Alkylation of XE-305 with 5-Chloromethyl-8-hydroxyquinoline (see Table I)

**Method (1)—With Excess Nitrobenzene (Ordinary Procedure).** Two g XE-305 was reacted with 1.38 g (6 mmoles) 5-chloromethyl-8-hydroxyquinoline hydrochloride in 15 ml nitrobenzene containing 10.8 mmoles aluminum chloride at 70°C for 48 hr. The polymer was immersed in methanol, filtered and washed with CH₃OH:HCl (1:1), CH₃OH, and ether, then dried at 70°C for 24 hr to yield 2.5 g polymer 1, (KW-37) with perfect round shape (see Fig. 1) with 1.51% nitrogen and 3.10% chlorine.

**Method (2)—Without Excess Nitrobenzene (Dry Procedure).** Two g XE-305 was reacted with 1.38 g (6 mmoles) 5-chloromethyl-8-hydroxyquinoline hydrochloride in 6 ml nitrobenzene containing 10.8 mmoles aluminum chloride at 70°C for 72 hr. Work-up yielded 2.7 g polymer 2 (KW-55) with perfect round shape, with 0.64% nitrogen and 4.7% chlorine.

**Method (3)—Impregnation From Chloroform.** 5-Chloromethyl-8-hydroxyquinoline hydrochloride, 1.4 g (6 mmoles), was dissolved in 60 ml water. Excess sodium bicarbonate (2 g) was added in portions, and the resulting precipitate was extracted with 3 × 50 ml CHCl₃. The extract was dried over anhydrous Na₂SO₄ and the solvent evaporated to the smallest volume before crystallization occurs. Two g dry XE-305 was added and, after a 1-hr swelling period, removed by distillation. Fresh CHCl₃ was added in a minimum amount

to redissolve crystals of 5-chloromethyl-8-hydroxyquinoline precipitated on the surface of the vessel. Two or three repetitions of this procedure produced 3.1 g free-flowing beads of perfect round shape impregnated with the ligand. Aluminum chloride (6 ml of 1.8$M$) in nitrobenzene was added, and the alkylation proceeded at 70°C for 72 hr. The polymer was worked up as described above to yield 3.1 g polymer 3 (KW-57) of twisted shape. (see Fig. 2) containing 1.79% nitrogen and 8.26% chlorine.

**Method (4)—Impregnation Followed by Acidification.** The impregnation procedure described in method (3) was followed to the point of free-flowing beads. The polymer was then placed in a column and dry HCl gas was passed for 10 min to yield the 5-chloromethyl-8-hydroxyquinoline hydrochloride-impregnated polymer. The polymer was placed in 6 ml 1.8$M$ aluminum chloride in nitrobenzene at 70°C for 72 hr. The usual work-up produced 3.1 g polymer 4 (RS-75) of the twisted type (see Fig. 3) containing 0.49% nitrogen and 7.42% chlorine. Similarly, polymers 5 and 6, prepared at 25°C and 150°C, respectively, were obtained. They also have the twisted shape.

### Alkylation of XAD-2 and XAD-4 with 5-Chloromethyl-8-hydroxyquinoline Hydrochloride (see Table I)

The alkylation was performed on 2-g samples of dry polymers according to method (3) described above. Polymers of ordinary round shape were obtained (see Fig. 4).

### Impregnation of XE-305 with 8-Hydroxyquinoline

8-Hydroxyquinoline, 1.0 g, was dissolved in 3 ml CHCl$_3$, followed by 2 g XE-305. Since all the solvent was taken up immediately by the polymer, fresh solvent was added to saturate the polymer. After 60 min, excess solvent was removed by evaporation. Aluminum chloride (2 ml of 1.8$M$) in nitrobenzene was added and the mixture left for 11 hr at 70°C. A sample was placed in methanol and filtered. The beads examined under the microscope had a twisted shape. After 72 hr, the polymer was filtered, washed with CH$_3$OH, 1:1 CH$_3$OH:HCl, methanol, water, methanol, and chloroform. The polymer was dried under vacuum to yield 1.84 g containing 0.4% nitrogen and 0.03% chlorine. The shape of the beads is back to regular spherical (AD-395).

### Metal Complexation Experiments

One-gram polymer samples were equilibrated for 24 hr in 20 ml 0.05$M$ CuSO$_4$ (pH = 4) and 0.05$M$ Fe$_2$(SO$_4$)$_3$ (pH = 2) solutions. The metal concentrations in the solutions were determined by atomic absorption spectroscopy and the metal uptake on the polymers calculated.

# References

1. F. Helfferich, *Ion Exchange,* McGraw-Hill, New York, 1962.

2. Y. Marcus and Kertes, D. S., *Ion Exchange and Solvent Extraction,* Wiley–Interscience, New York, 1969.

3. R. Kunin, E. F. Meitzner, and N. Bortnick, *J. Am. Chem. Soc.,* **84,** 305 (1962).

4. J. A. Mikes, in *Ion Exchange in the Process Industries,* S.C.I. Conference, Imperial College, 1970, p. 16.

5. T. R. E. Kressman, in *Ion Exchange in the Process Industries,* S.C.I. Conference, Imperial College, 1970, p. 3.

6. A. Warshawsky, R. Kalir, and A. Patchornik, *J. Org. Chem.,* **43,** 3151 (1978).

7. S. Sano, R. Tokunaga, and K. A. Kun, *Biochim. Biophys. Acta,* **244,** 201 (1971).

8. D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.,* **94,** 9284 (1972).

9. G. Schmuckler and S. Goldstein, in *Ion Exchange and Solvent Extraction,* Vol. 7, J. Marinsky and Y. Marcus, eds., Marcel Dekker, New York, 1977.