further purification. $AlCl_3$ was purified by repeated sublimation under HCl. $AlEt_2Cl/AlCl_3$ was prepared by reaction of $AlEt_2Cl$ with the equimolar amount of $AlCl_3$ in toluene.

**Measurements.** Nmr spectra were taken with a Varian Model A-60 spectrometer (60 Mc). All the polymer and the dialkoxyphthalans spectra were obtained as solution of approximately 1 mol (per unit) per liter at about 40° against TMS standard in a capillary. Molecular weights were measured with a vapor pressure osmometer (Mechrolab Model 301 A) in benzene at 37°. Viscosity determinations were carried out at 30° in benzene by using an Ubbelohde dilution-type viscometer.

**Acknowledgment.** We are grateful to Dr. T. Kunitake of our research group for many valuable discussions. C. A. is also grateful to Professor G. B. Butler of the University of Florida and Dr. R. M. Ottenbrite, then at the University of Florida, for their assistance in preparing the preliminary manuscript[1] on the basis of which this paper was written.

# Polymers with Chelated Polyquinoxaline Segments

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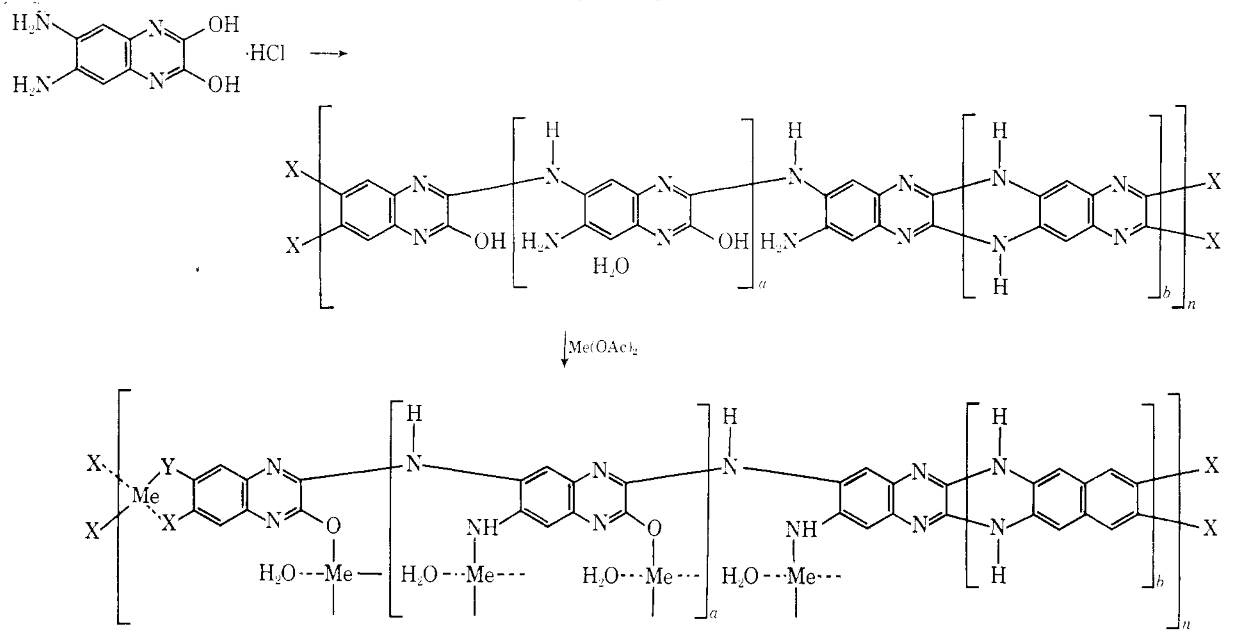
ABSTRACT: Polymeric chelates between polyquinoxaline prepolymers and copper, nickel, and cadmium acetates have been synthesized. The copper chelate showed better high-temperature stability than the high molecular weight polytetraazaanthracene. The ac and dc conductivities of the chelates increased with the increasingly covalent nature of the organic ligand–metal bond. Esr studies on the monomers and prepolymers showed the presence of free radicals and from their fine structure spectra an assignment to the appropriate anion radicals was made.

There are two major methods available for building chelate polymers with metal ions. One of the methods involves the use of polyfunctional monomers which on reaction with a metal ion or salt produce the polymer. The other involves first the synthesis of a polymer which has repeating units that can react with a metal ion to then form the polymeric chelate. One can visualize also a third approach which combines the above two and was the goal of this work in the preparation of polymeric chelates containing the basic polyquinoxaline segment as a part of the polymer chain. This was accomplished by first synthesizing polyquinoxaline "prepolymers" of low enough molecular weight so that they were completely soluble in organic solvents, and then follow by the polychelation reaction with copper, nickel, and cadmium acetates. The type of structures obtained are illustrated in Scheme I. Spectroscopic (ir, uv, and esr) studies were conducted on the chelated materials and they were evaluated for thermal and conductivity properties.

SCHEME I



$a$ = number of repeat units in one segment
$b$ = number of repeat units in the other segment
X, Y = end groups, not determined

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[1] (a) Author to whom correspondence should be addressed. (b) On leave of absence from Ranchi University, Ranchi, India.

TABLE I
MONOMERS AND CHELATED AND UNCHELATED POLYQUINOXALINES

| | Polym-erizn temp, °C | Polym-erizn time, hr | % convn | $\eta_{inh}$[a] | Calcd, % | | | | | Found, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | Cl | O | C | H | N | Cl | O |
| $C_8H_8O_2N_4 \cdot 2HCl \cdot H_2O$ (as received) | | | | | 33.95 | 4.27 | 19.78 | 25.04 | 17.00 | 33.93 | 4.10 | 20.09 | 25.79 | |
| $C_8H_8O_2N_4 \cdot HCl$ | | | | | 38.94 | 4.50 | 22.71 | 14.37 | 14.00 | 38.73 | 4.61 | 22.56 | 14.54 | |
| High mol wt polymer | 250 | 24 | 66 | 0.84 | 61.52 | 2.58 | 35.88 | | | 59.66[b] | 2.60[b] | 34.51[b] | | |
| Low mol wt polymer, bulk | 355 | 9 | 71 | 0.19 | 50.00 | 4.21 | 29.13 | | 16.64 | 50.44 | 4.19 | 29.11 | | 19.32 |
| Low mol wt polymer, soln | 200 | 1 | 49 | 0.14 | 50.00 | 4.21 | 29.13 | | 16.64 | 50.63 | 3.81 | 29.30 | | 15.56 |
| Cu chelate | ~200 | 24 | | | 28.66 | 2.41 | 16.70 | | 14.32 | 26.77 | 2.25 | 14.18 | | |
| Ni chelate | ~200 | 24 | | | 29.51 | 2.49 | 17.20 | | 17.81 | 31.84 | 2.74 | 14.60 | | |
| Cd chelate | ~200 | 24 | | | 22.19 | 1.87 | 12.93 | | 11.09 | 27.50 | 1.89 | 11.66 | | |

[a] Determined on solutions of 0.473–0.504 g/100 ml of methanesulfonic acid. [b] Data of Marvel, *et al.*, ref 2.

## Experimental Section

**Monomers. 2,3-Dihydroxy-6,7-diaminoquinoxaline Monohydrochloride.** The monohydrochloride was obtained from the dihydrochloride monohydrate by dissolving it in hot water and then reprecipitating in dilute (~3%) hydrochloric acid upon cooling and drying in a vacuum oven at room temperature for 24 hr. The material did not have a melting point below 520°.

**2,3-Dihydroxy-6,7-diaminoquinoxaline Dihydrochloride Monohydrate.** This monomer was used as received from Burdick and Jackson Labs, Inc. See Table I for analytical data.

**Typical Polymerizations.** The self-condensation procedure of Marvel, *et al.*,[2] was used in the syntheses of the polymers. The use of the dihydrochloride monohydrate gave excellent yields of the higher molecular weight ($\eta_{inh}$ 0.84, 0.550 g/100 ml of methanesulfonic acid) polymers. To obtain the lower molecular weight ($\eta_{inh}$ below 0.3) polymers the heating cycle had to be changed considerably. The use of the monohydrochloride was also explored in these preparations with good results. Only polymers with $\eta_{inh}$ below 0.3 were completely soluble in hexamethylphosphoramide (HMP) and less so in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The higher molecular weight polymers ($\eta_{inh}$ >0.3) were soluble in HMP to the extent of a few per cent and we estimate less than 1% in DMF and DMSO. All polymers were completely soluble in sulfuric and methanesulfonic acids.

**Solution Polymerization. Polyphosphoric Acid.**[3] The polyphosphoric acid was always freshly prepared by placing 100 g of $P_2O_5$ in a round-bottomed, three-necked flask, placed in an ice bath, and adding 20 ml of deionized water over a 30-min period while stirring. Upon completion of addition of the water, the flask was placed in a wax bath and the temperature was adjusted to 120° and then maintained for 24 hr.

**High Molecular Weight Polymer.** The dihydrochloride monohydrate (5 g) was slowly charged under nitrogen at 120° in the freshly prepared polyphosphoric acid. This was followed by a heating cycle of 1 hr at 150° and then 24 hr at 250°. The resulting viscous solution, while still hot (~150°), was poured into 800 ml of 10% ammonium hydroxide solution and the pH was adjusted to just basic (litmus paper). The mixture was allowed to stand overnight, and the collected polymer was extracted with water for 72 hr followed by methanol for 72 hr. The material was dried in a vacuum oven at 120°/24 hr. Black powder, 2.5 g (50%), $\eta_{inh}$ 0.84 (0.470 g/100 ml of methanesulfonic acid), essentially completely soluble in sulfuric and methanesulfonic acids, was isolated. The product obtained has been postulated,[2b] in accordance with the analytical data, to contain a high yield of the condensed ring structure shown inside the brackets with subscript *b* in the formula given in Scheme I.

**Low Molecular Weight Polymer.** To obtain polymers with inherent viscosity less than 0.3 the polymerization temperature was raised directly from 120 to 200° and maintained for not more than 1 hr. Drying of the isolated polymer in a vacuum oven at room temperature for 24 hr yielded typically about 50% of a dark brown powder of $\eta_{inh}$ 0.15. The theoretical analysis for this as well as the bulk polymerization product was calculated for the structure shown inside the brackets with subscript *a* in the formula given in Scheme I.

**Bulk Polymerization.** The monohydrochloride (0.60 g) was placed under nitrogen in a two-necked round-bottomed flask connected to a trap containing copper sulfate solution. The flask was then immersed in a 230° salt bath and the temperature was raised to 330° and maintained for 15 hr followed by 355°/9 hr. No traces of ammonia gas seemed to be given off. The reaction mixture was extracted with dimethylacetamide and the product was dried in a vacuum oven at 90°/24 hr. Dark brown powder, 0.41 g (71%), $\eta_{inh}$ 0.19 (0.498 g/100 ml of methanesulfonic acid), was isolated. The material was completely soluble in methanesulfonic acid and less so in HMP.

**Chelation.** The polyphosphoric acid prepared low molecular weight polyquinoxaline (1.0 g) was combined with HMP (50 ml) in a round-bottomed flask and the mixture was refluxed for 24 hr. At the end of this period only traces of undissolved material remained. The solution was filtered and the filtrate was combined with an aqueous solution of copper (nickel, cadmium) acetate (140 ml of 0.1 *M*). The solution was then refluxed for 24 hr at which time a heavy dark brown precipitate had formed. The filtered material was washed with three 50-ml portions of tetrahydrofuran and then dried in a vacuum oven at 170°/72 hr. Dark brown powder (1.40 g) was isolated.

## Results and Discussion

**Polymerization Studies.** Some of the experimental conditions and results are summarized in Table I. We were unable to prepare lower than $\eta_{inh}$ 0.35 materials using the heating cycle of the high molecular weight polymers for as short a polymerization time as 30 min. None of these materials possessed sufficient solubility in

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(2) (a) H. Jadamus, F. De Schryver, W. De Winter, and C. S. Marvel, *J. Polym. Sci., Part A-1*, **4**, 2831 (1966); (b) F. De Schryver and C. S. Marvel, *ibid., Part A-1*, **5**, 545 (1967).

(3) C. S. Marvel, personal communication.

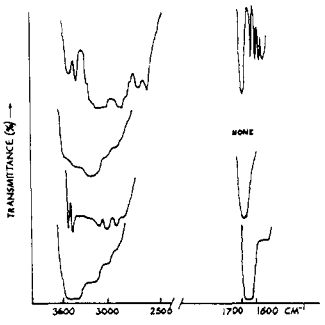

Figure 1. Some of the major changes in the absorption peaks at 2600–3600 and 1630–1690 cm$^{-1}$ in the monomer, high and low molecular weight polymers, and copper chelate —from top to bottom: $C_8H_8O_2N_4 \cdot 2HCl \cdot H_2O$, essentially **1**, essentially **2**, and copper chelate.

HMP, DMF, or DMSO although they were completely soluble at room temperature in sulfuric and methanesulfonic acids. By lowering the polymerization temperature to 200° and decreasing the polymerization time to 1 hr, polymers of $\eta_{inh}$ below 0.2, which were completely soluble in hot HMP, were consistently obtained. The other approach involved bulk condensation of the quinoxaline monohydrochloride. Bulk condensation gave considerably higher yields of the polymer as compared to the polyphosphoric acid technique.

Satisfactory analytical data on heterocyclic thermostable polymers are difficult to obtain. Polyquinoxaline is no exception to this, as the data of Marvel, *et al.*,[2] showed it. In our preparation of the low molecular weight materials incomplete ring closure was expected. We do not have information as to the exact proportion of the cyclized *vs.* uncyclized segments in these polymers; however, the esr data, as described later, suggest that the polymer has largely the uncyclized structure. The analytical data also confirmed this and indicated that there was one molecule of water of hydration per repeating unit. As the chelates were hygroscopic and intractable, purification was not very effective and the analytical data were erratic. Similar experience with hygroscopic chelates has been reported by Marvel, *et al.*[4,5]

**Spectroscopic Studies. Infrared Absorptions.** All the data were obtained on KBr disks. Some of the major changes in the absorption peaks at 2600–3600 and 1630–1690 cm$^{-1}$ in the monomer, high and low molecular weight polymers, and copper chelate are illustrated in Figure 1. Identification of systematic trends in the 2600–3600-cm$^{-1}$ region, characteristic of OH, NH, CH stretching, could not be made because of the presence of a multitude of strong overlapping peaks. However, one major change was easily observed: the lower frequency absorptions (2600 cm$^{-1}$ and up) were progressively eliminated in going from the monomers to the low molecular weight polymers, to high molecular weight polymer, and finally, the chelated polymers. The broad strong absorptions in the 2500–2850-cm$^{-1}$ region have been assigned to hydrogen bonded NH groups in the case of resorcinoldicarboxaldehyde-*o*-phenylenediamine polymers.[6] These absorptions were absent in the Cu chelates of those polymers. Similar assignment can be made to our chelated and unchelated polymers. The low frequency absorption which started at 2600 cm$^{-1}$ in monomers was shifted to 2800 cm$^{-1}$ in the low molecular weight polymer, to 3080 cm$^{-1}$ in the high molecular weight polymer, and to 3100 cm$^{-1}$ in the chelates. The strong absorption at 1690 cm$^{-1}$ in the monomers and 1680 cm$^{-1}$ in the low molecular weight polymer is broadened out and resolved into a lower frequency doublet in the chelates. The shift to lower frequency is consistent with the proposed chelate structure in which the metal atoms react with the available OH and $NH_2$ groups. There are no changes in the absorption spectrum of the low molecular weight polymer refluxed in HMP without the addition of the chelating metal.

TABLE II
THERMOGRAVIMETRIC DATA ON CHELATED AND UNCHELATED POLYQUINOXALINES

| Samples | $\eta_{inh}$ | Temp, °C, at 10% wt loss | | Temp, °C, at 50% wt loss | |
|---|---|---|---|---|---|
| | | Air | $N_2$ | Air | $N_2$ |
| High mol wt polymer | 0.84 | 470 | 610 | 570 | 866 |
| Low mol wt polymer, bulk | 0.19 | 383 | 415 | 457 | 695 |
| Low mol wt polymer, soln | 0.16 | 387 | 402 | 465 | 693 |
| Cu chelate | | 350 | 380 | 660 | 853 |
| Ni chelate | | 340 | 340 | 425 | 677 |
| Cd chelate | | 358 | 390 | 575 | 705 |

**Ultraviolet Absorptions.** Sulfuric acid was used as a solvent because of the insolubility of the high molecular weight and chelated polymers in nonacidic solvents. Although spectra with many peaks in the 190–600-m$\mu$ region could be obtained it was soon noticed that the spectra were sensitive to dissolution conditions and the length of time the sample was allowed to stand. No correlations are attempted therefore.

**Thermogravimetric Studies.** Thermogravimetric analysis was performed in air and in nitrogen at a heating rate of 5°/min. Some of the data are listed in Table II. The thermal stability of our high molecular weight polymer ($\eta_{inh}$ 0.84 was comparable to that of Marvel's.[2b] The low molecular weight polymers had considerably lower thermal stabilities in air and $N_2$ in agreement with the single-strand nature of these polymers. The thermal stability of polymeric chelates is dependent upon great many factors among which the metal, the organic ligand, and their stereochemistry are important. In the case of the three chelated polymers here the only variable has been the metal ion. Presumably, all three metal ions form the square planar chelate structure. The thermogravimetric data indicated the following: (1) the chelates did contain a tightly bound water of hydration which was lost between 300 and 400°, (2) the copper chelate had a better high-temperature stability in air and about the same in $N_2$ as the high molecular weight ($\eta_{inh}$ 0.84) polymer, (3) the cadmium chelate had the same high-temperature stabil-

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(4) C. S. Marvel and N. Tarkoy, *J. Amer. Chem. Soc.*, **80**, 832 (1958).

(5) C. S. Marvel and P. V. Bonsignore, *ibid.*, **81**, 2668 (1959).

(6) T. Lebsadze, K. A. Chkhartishvili, I. Y. Pavlenishvili, and M. T. Gugava, *Vysokomol. Soedin., Ser. B*, **10** (8), 609 (1968).

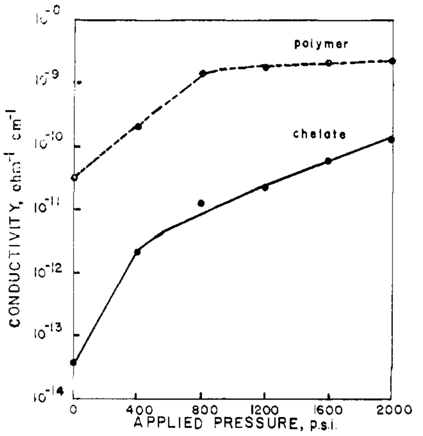


Figure 2. Dc conductivity as a function of pressure applied upon the sample.

ity in air and not as good in $N_2$ as the high molecular weight polymer, and (4) the nickel chelate showed no improvement over the unchelated polymer and was appreciably worse than the high molecular weight polymer. The fact that the *initial* water lost in the thermogravimetric analysis from the chelates was the water of hydration rather than that from the ring closure is evident from the comparatively low temperature at the 10% weight loss for these materials.

**Conductivity Studies.** Great difficulties exist in the interpretation of the conductivity measurements in polymeric solids because of the highly impure and highly disordered nature of such materials in general. Some of these problems and suggestions of experimental nature have been discussed recently.[7-9] Thus, it should be made clear from the beginning that because of the complex nature of the polymeric materials studied here the conductivity data presented can be only of qualitative significance. Both ac and dc resistance measurements have been made at room temperature in air and in nitrogen and the dc measurements also as a function of the applied pressure upon the sample. Some of the details of our experimental procedure are given first. The pellets were prepared by placing from 0.1 to 0.2 g of the samples into a KBr pellet press, applying 2800 psi at room temperature, followed by a 2–3 hr cycle at 145° in an oven and then compressing again to 2800 psi for at least 1 min. The pellets were placed in a vacuum oven at 60° for about 16 hr just before evaluation. They were either used as such in a guarded ring electrode assembly (Balsbough Laboratories three-terminal strip electrode system, Type ES 100-24-3T50GR) or by applying a conductive silver paint (E-kote 40) electrodes first and then mounting in a shielded cell between two spring loaded copper leads tipped with E-type 3042 silver epoxy paint.

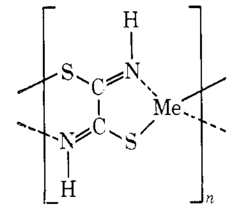
The resistances were measured with the following instruments: (1) General Radio Co. 1311 audio oscillator, Type 1232-A tuned amplifier and null detector, and a 1615 capacitance bridge, (2) Boonton Radio Corp. Q Meter, Type 260-A, and (3) General Radio Corp. dc amplifier and electrometer, Type 1230-A. The dc resistances were measured at 9.1 V (internal electrometer voltage) with the passage of direct current for different times, and also the direction of current flow reversed.

Table III

| | Ac, in air guard ring, $ohm^{-1}$ $cm^{-1}$ | Dc in $N_2$, atm pressure $ohm^{-1}$ $cm^{-1}$ |
|---|---|---|
| Unchelated polymer | $2.6 \times 10^{-9}$ | $5.0 \times 10^{-11}$ |
| Cu chelate | $8.4 \times 10^{-10}$ | $5.4 \times 10^{-14}$ |
| Ni chelate | $3.4 \times 10^{-10}$ | $5.9 \times 10^{-15}$ |
| Cd chelate | $2.6 \times 10^{-10}$ | $5.0 \times 10^{-16}$ |

The unchelated polymers had the following ac conductivities at 10 kcal in air in the guard ring electrode assembly: (1) high molecular weight polymer, $9.3 \times 10^{-9}$ $ohm^{-1}$ $cm^{-1}$, (2) low molecular weight polymer, prepared in polyphosphoric acid, $2.6 \times 10^{-9}$ $ohm^{-1}$ $cm^{-1}$, and (3) low molecular weight polymer prepared in bulk, $1.8 \times 10^{-10}$ $ohm^{-1}$ $cm^{-1}$. The higher conductivity of the polyphosphoric acid prepared low molecular weight as compared to bulk prepared polymer suggest that possibly polyphosphoric acid has contributed to this. The three chelated polymers and the unchelated material from which they were made had the ac (at 10 kcal) and dc conductivities given in Table III.

Interestingly, the same order of conductivities (copper chelate the highest, followed by nickel and then cadmium) has been found also for the polyrubeanates in which the metal–sulfur bond was present in the structure[10]



Furthermore, this is also the order of increasing electropositive character of the metal ions, copper being the most electronegative.[11,12] Thus, the increase in conductivity in these particular chelate polymers is favored by the increasingly covalent nature of the organic ligand–metal bond.

The dc data as a function of pressure applied upon the sample have been plotted in Figure 2. In the rather small pressure region studied, from 0 to 2000 psi, the conductivity for the unchelated sample seemed to level off around $3 \times 10^{-9}$ $ohm^{-1}$ $cm^{-1}$ while that of the copper chelate was still increasing, although at a slower rate. This difference was probably due to the quality of the pellets as it was considerably more difficult to form a good pellet from the chelates. The dc conduc-

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(7) C. M. Huggins and A. H. Sharbaugh, *J. Chem. Phys.*, **38**, 393 (1963).

(8) A. G. Hankin and A. M. North, *Trans. Faraday Soc.*, **63**, 1525 (1967).

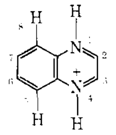
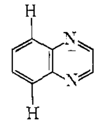
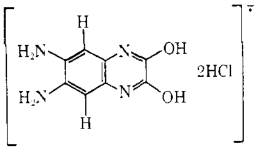
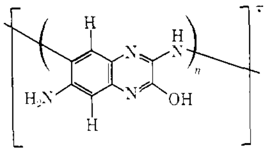
(9) M. M. Labes, paper presented to the Division of Organic Coatings and Plastics Chemistry, the 153rd Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Preprints, **27**, 18 (1967).

(10) A. P. Terentev, V. M. Vozzhennikov, Z. V. Zvonkova, and L. I. Badzhadze, *Dokl. Akad. Nauk SSSR*, **140** (5), 1093 (1961).

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 88.

(12) W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

TABLE IV
ESR DATA ON MONOMERS AND LOW MOLECULAR WEIGHT POLYMER

| Radical | Hyperfine splitting | | | | |
|---|---|---|---|---|---|
| | $a_{N1,4}$ | $a_{H2,3}$ | $a_{H5,8}$ | $a_{H6,7}$ | $a_{N-H}$ |
| <br>Dihydroquinoxaline cation[a] | 6.65 | 3.99 | 0.78 | 1.38 | 7.17 |
| <br>Quinoxaline anion[b] | 5.64 | 3.32 | 2.32 | 1.00 | |
| <br>Monomer (seven-line spectrum) 2N + 2H, present studies | 4.6 | | 4.05 | | |
| <br>Polymer (seven-line spectrum) 2N + 2H, present studies | 4.6 | | 4.05 | | |

[a] See ref 14. [b] See ref 15.

tivity data were practically duplicated by decreasing the pressure in steps back to atmospheric and then again increasing.

**Esr Studies.** The spectra were recorded as first derivatives of absorption curve with the Varian 4502-10 spectrometer using 100-Kc field modulation. The $g$ values and the number of unpaired spins were determined by comparison with that of Varian Standard "Pitch" sample.

The chelated as well as the unchelated polymers all gave a very strong single line ($\Delta H \cong 5$ G) spectrum ($g = 2.0028$, Figure 3). The single line of the low molecular weight polymer was also present in solution (concentrated sulfuric acid). The number of free spins in all cases was found to be in the neighborhood of $10^{17}$ spins/g. Although the site of unpaired electrons in the polymer could not be deduced directly from the single line spectrum, it is possible that due to the highly conjugated system (in the polymer) we are not able to see any hyperfine structure. The monomer did show a faint signal which could not be removed by recrystallization and this was taken into account when calculating the intensity and the number of spins in the case of polymers. The copper chelate gave an unsymmetrical single line spectrum displaced to lower field ($g \approx 2.25$, Figure 4), which therefore, constitutes an independent evidence for chelate formation.[13]

Hexamethylphosphoramide, an inert solvent, was also used to resolve any fine structure spectra. To our surprise, both the monomer and the low molecular weight polymer gave well-resolved spectra. Comparison of the results of present studies with the previously reported values for dihydroquinoxaline cation[14] and quinoxaline anion[15] radicals strongly suggest that the radicals are the radical anions of the monomer and the polymer. Treatment of monomer with cold HMP gave a seven-line spectrum of relative intensity 1.2:5:9.2:11.6:9.2:9:1.5, with 4.6 G separation between these lines (Figure 5). This can be understood in terms of hyperfine splitting from two nitrogens (1,4) and two protons (5,8). The two nitrogens in position 1 and 4 give a five-line spectrum of relative intensities 1:2:3:2:1, each of which is further split into three lines of equal splitting due to the protons (2) in positions 5 and 8 (Table IV). The relative intensity for such a spectrum

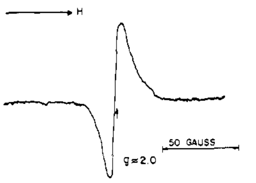


Figure 3. Esr spectrum of the chelated and unchelated polymers at 25°.

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(13) A. Abragam and M. H. L. Pryce, *Nature*, **163**, 992 (1949).

(14) B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 1455 (1964).

(15) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

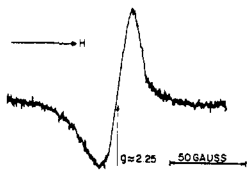


Figure 4. Esr spectrum of the copper chelate at 25°.

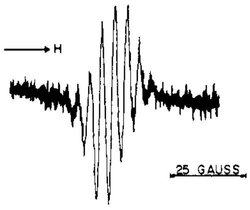
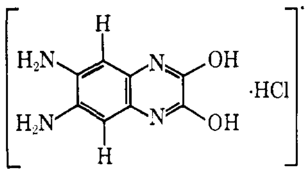


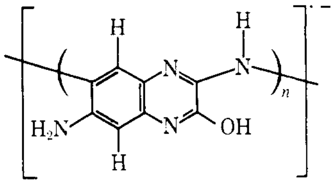
Figure 5. Esr spectrum of 2,3-dihydroxy-6,7-diaminoquinoxaline dihydrochloride monohydrate in cold hexamethylphosphoramide at 25°.

should be 1:4:8:10:8:4:1. The theoretical intensity is not significantly different from the one which is being observed. The radical responsible for this spectrum is therefore proposed to be



To the best of our knowledge this is the first time that a free radical formation has been observed in a HMP solution of an organic heterocyclic compound and also its low molecular weight polymer. We can not offer a definite explanation for this at this time except to suggest that a possible charge-transfer complex formation may have occurred. More detailed studies are underway. It should be added that HMP itself gave no signal under identical experimental conditions.

The low molecular weight polymer in HMP also gave a seven-line spectrum (Figure 6), identical with that of rhe monomer. On the basis of these results, the only ieasonable structure which can be assigned to the radtcals is



which is also in agreement with the other evidence for the predominantly uncyclized structure for this polymer.

A further observation during these studies was that solutions of the monomer in DMSO changed color with heating. The sequence of color changes was almost identical with that observed in polymerization. Solutions of monomer in cold DMSO were yellow and showed no signal. As the solution was heated the color changed to orange and then deep red. The red solution was paramagnetic and gave a nine-line spectrum (Figure 7). A vigorous heating produced a dark brown-to-black solution which did not show any signal. The nine-line spectrum suggested equal interaction of the unpaired electrons with two nitrogens and four protons. A reasonable structure of this radical is proposed to be

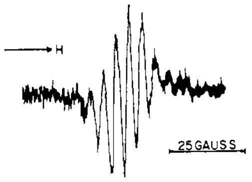


Figure 6. Esr spectrum of the low molecular weight polymer in hexamethylphosphoramide at 25°.

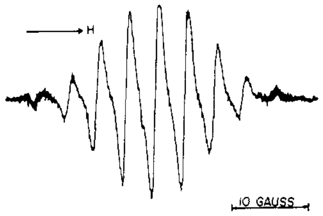
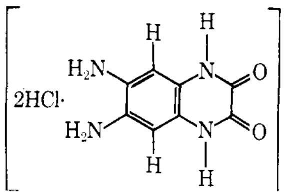


Figure 7. Esr spectrum of 2,3-dihydroxy-6,7-diaminoquinoxaline dihydrochloride monohydrate in dimethyl sulfoxide after warming and at 25°.



It has been observed before that the 2,3-dihydroxyquinoxaline exists largely in the keto form.[2a]

The observed spectrum consists of nine lines of relative intensities 1:6:15:23:30:23:15:6:1, with a 4.1-G separation between the lines. The theoretical relative intensities according to this scheme should be 1:6:17:30:36:30:17:6:1. The observed spectrum is not very different from the theoretically predicted one; hence, we suggest the above structure for the radical. Treatment of tetracyanoethylene (TCNE) with DMSO has been recently shown to result in the formation of TCNE radical anion.[16] These results relate to our observations of the radical-anion formation in DMSO. It is important to note that the presence of these radical anions in solutions of DMSO involve a rather complex sequence of events as noted by Symons, *et al.*[16]

Because of the identical color changes in the DMSO solution of monomer and the polymerization reaction mixture with heating and the accompanying appearance of a free radical in the DMSO solution, it was of interest to monitor the polymerization reaction with parallel esr studies. Samples of the polymerization mixture were withdrawn at various time intervals during the polymerization, however, at no stage was any signal detected. This would indicate that either the radical concentration was too low for detection by esr or that the

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(16) R. N. Butler, J. Oakes, and M. C. R. Symons, *J. Chem. Soc.*, A, 1134 (1968).

reaction was a simple condensation reaction.

Gamma irradiation (Co 60, 1500 Cu) of the chelated and unchelated polymers at a dose rate of 0.35 Mrad/hr up to a total dose of 85.1/Mrads at room temperature in air produced essentially no change in the esr signal, thus demonstrating the exceptional resistance of these polymers to high energy radiation. While there was practically no change in the viscosity in the high molecular weight polymer the viscosity of the low molecular weight polymer in one case had increased by 100%.

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# The Control of Copolymer Composition Distributions in Batch and Tubular Reactors

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ABSTRACT: In this paper, the problem of maintaining a specified copolymer composition distribution in a batch reactor is considered. The advantages of temperature control, rather than monomer addition are discussed, and the necessary and sufficient conditions for temperature control in the face of monomer depletion are derived. Examples are worked to illustrate the results for a practical range of temperatures.

In this paper we are considering the composition of a copolymer resulting from polymerization carried out in a batch or plug-flow tubular reactor. If the reactants are well mixed initially, the temperature is considered uniform in the reactor at every residence time, and the chain length is very long, then the composition of polymer produced at any instant in the reactor can be represented by[1]

$$F_1 = \frac{(r_1 - 1)f_1^2 + f_1}{(r_1 - r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \qquad (1)$$

where $F_1$ = mole fraction of monomer $M_1$ polymer, $f_1$ = mole fraction of monomer $M_1$ in solution = $M_1/(M_1 + M_2)$, $r_1$ = reactivity ratio of monomer $M_1 = k_{11}/k_{12}$, $r_2$ = reactivity ratio of monomer $M_2 = k_{22}/k_{21}$, and where the $k_{ij}$ are the propagation rate constants for the propagation steps

$$P_{n,m} + M_1 \xrightarrow[k_{11}]{} P_{n+1,m}$$

$$P_{n,m} + M_2 \xrightarrow[k_{12}]{} Q_{n,m+1}$$

$$Q_{n,m} + M_2 \xrightarrow[k_{22}]{} Q_{n,m+1}$$

$$Q_{n,m} + M_1 \xrightarrow[k_{21}]{} P_{n+1,m}$$

where $P_{n,m}$ = concentration of growing polymer with terminal $M_1$ and $Q_{n,m}$ = concentration of growing polymer with terminal $M_2$.

Equation 1 has been integrated[2,3] for isothermal batch reactors with depletion of monomer to give the copolymer composition distribution (CCD) under these conditions. Except for the rare case where $M_1$ and $M_2$ disappear in such a way that $f_1$ remains constant, the CCD will not be monodisperse due to variations in $f_1$ with total monomer conversion. O'Driscoll and Knorr[3,4] aptly illustrate the CCD which can be expected in these cases.

If one wished to produce a polymer with monodisperse CCD, he could (i) add additional amounts of the most reactive monomer as the reaction progresses to maintain $f_1$ constant, or (ii) adjust the reactor temperature (which affects the values of $r_1$ and $r_2$) so as to keep $F_1$ constant in the face of changes in $f_1$. Control scheme i is quite simple conceptually and would only require careful addition of one monomer species, but suffers from the requirement that the added monomer must be perfectly mixed with the (often quite viscous) polymer in order to produce a monodisperse CCD. Any imperfections in the mixing will produce a widened CCD.[3,4] Control scheme ii is not as simple conceptually (as it requires the selection of a temperature at each $f_1$ to give the correct combination of $r_1$ and $r_2$ for constant $F_1$) and in fact will not always work for all systems. Nevertheless it has the enormous practical advantage that no material is added to the polymer so that only temperature uniformity is required at all times. Since it is much easier to design reactors for very viscous materials with good temperature control than with perfect micromixing, control scheme ii looks very attractive indeed.

In this paper we will first explore the range of values of $F_1$, $f_1$, over which temperature control is possible, then give simple graphical techniques for computing these parameters for each $f_1$, and finally treat some ex-

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(1) I. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).

(2) V. Meyer and G. Lowry, *J. Polym. Sci., Part A*, 3, 2843 (1965).

(3) K. F. O'Driscoll and R. Knorr, *Macromolecules*, 1, 367 (1968).

(4) K. F. O'Driscoll and R. Knorr, paper presented at A.I.Ch.E. Meeting, Cleveland, Ohio, May 1969.