prepared in the appropriate solvent. One milliliter aliquots were sealed in tubes and heated at 130 or 150°. Tubes were quenched in ice water at various intervals, their contents poured into 20 ml of water, the products extracted with three 4-ml portions of pentane, and the combined extracts dried and concentrated. The residues were analyzed by glpc using a 2-ft 15% diethylene glycol succinate on Chromosorb W column. At 120° and a helium carrier flow of 50 ml/min, **6** and **7** showed retention times of 14.0 and 8.2 min, respectively. The analogous deuterated compounds **10** and **11** gave similar results on this column. Isomerizations in the presence of potassium thiocyanate or potassium perchlorate were analyzed by the same procedure.

Deuterium Labeling Experiments. Solutions of **10** were made up in sulfolane, TMU, or diglyme using quantities such that at least 0.08 g of isothiocyanate would be produced after the isomerization interval. The appropriate solutions were sealed in glass tubes and heated at 150 ± 0.1°. Tubes were removed at various time intervals and worked up in the previously described manner. Separation of the crude isomerization mixture and analyses of the components were carried out as described before.

Isomerization of (−)-*exo*-2-Norbornyl Thiocyanate ((−)-6). A 1.029 g (6.73 mmol) sample of (−)-**6** was dissolved in 45 ml of sulfolane, sealed in a tube, and heated at 130 ± 0.1° for 8 hr (10.9% isomerization). The tube was quenched in ice water and worked up in the usual manner. Separation of the crude mixture on silica gel followed by distillation afforded pure thiocyanate and isothiocyanate, whose respective optical rotations were measured. This procedure was repeated with samples heated for 20.0, 35.0, and 57.0 hr (26%, 45%, and 77% reaction, respectively; see Table III).

Tracer Studies. A solution 0.1 *M* in potassium thiocyanate-^{35}S and in **6** was prepared by dissolving 3.81 mg of potassium thiocyanate-^{35}S (specific activity = 27.3 mCi/mmol), 96.09 mg of potassium thiocyanate, and 153 mg of **6** in 10 ml of sulfolane. One milliliter aliquots of the resultant solution were sealed under nitrogen in ten tubes and heated at 130.1°. The tubes were quenched at regular intervals (see Table IV). Extent of isomerization was measured by analysis of control tubes containing 0.1 *M* solutions of nonradioactive thiocyanate ion and **6**.

To each tube containing-^{35}S thiocyanate were added known amounts of unlabeled **6** and **7** as carriers. The resultant mixture was then poured into exactly 25.0 ml of water and extracted three times with 5-ml aliquots of pentane. The water solution was saved for analysis to determine the amount of remaining ionic ^{35}S thiocyanate.

The combined pentane extracts were washed two times with 5 ml of water, dried, and the solvent evaporated. The mixture activities reported in Table IV were determined from accurately weighed amounts of this purified product. To effect separation of thiocyanate and isothiocyanate, each mixture was then treated with aniline in a procedure analogous to that reported for preparing the 1-adamantylthiourea derivative of **7**. Work-up afforded **6** and 1-phenyl-3-*exo*-2-norbornylthiourea. The R-SCN activities reported were found by analyzing known weights of **6** recovered for the above reaction. Isothiocyanate activities were acquired from analyses of the aniline thiourea derivatives after their recrystallization from ether–pentane.

Activity of ionic thiocyanate was measured utilizing a 5 μl aliquot of each water sample. The remaining water solution was then extracted twice with ether, its volume measured, and another 5-μl sample analyzed. This procedure was repeated to constant activity.

Acknowledgments. We are grateful to the Petroleum Research Fund administered by the American Chemical Society (Grant No. 2925-Al) for partial support of this research. We also wish to thank Professors W. S. Brinigar and J. Stritar for their many helpful discussions.

Preparation and Characterization of Tyrosine and Lysine Metal Chelate Polyesters and Polyamides[1]

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Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received July 25, 1969*

Abstract: Polyesters and polyamides of bis(tyrosinato)metal(II) (M = Cu, Ni) and bis(lysine)metal(II) dichloride (M = Cu, Zn) complexes have been synthesized by interfacial polycondensation with aryl diacid chlorides. The presence of unhydrolyzed acid chloride end groups in the products indicates that the degree of polymerization is governed by the insolubility of the products in both phases. Using a semiquantitative determination of the organic compounds obtained upon removal of the metal ion, the degree of polymerization is estimated to be four to five. This removal has led to the characterization of the following new organic compounds: O,O′-2,5-dichloroterephthaloyldityrosine, O,O′-terephthaloyldityrosine, O,O′-isophthaloyldityrosine, ε-N,ε-N′-2,5-dichloroterephthaloyldilysine, ε-N,ε-N′-terephthaloyldilysine, and ε-N,ε-N′-isophthaloyldilysine.

There are three fundamentally different synthetic approaches which lead to chelate polymers: (1) the reaction of metal ions with bischelate ligands, (2) the chelation of metal ions by an existing polymer,[2-5] and (3) the polymerization of metal chelates containing free functional groups.[6,7]

We have used the third approach and the interfacial polymerization technique to prepare polyamides and polyesters of the general types I–IX. We have also determined the degree of polymerization by semiquantitative determination of the organic compounds obtained when the metal ion is removed.

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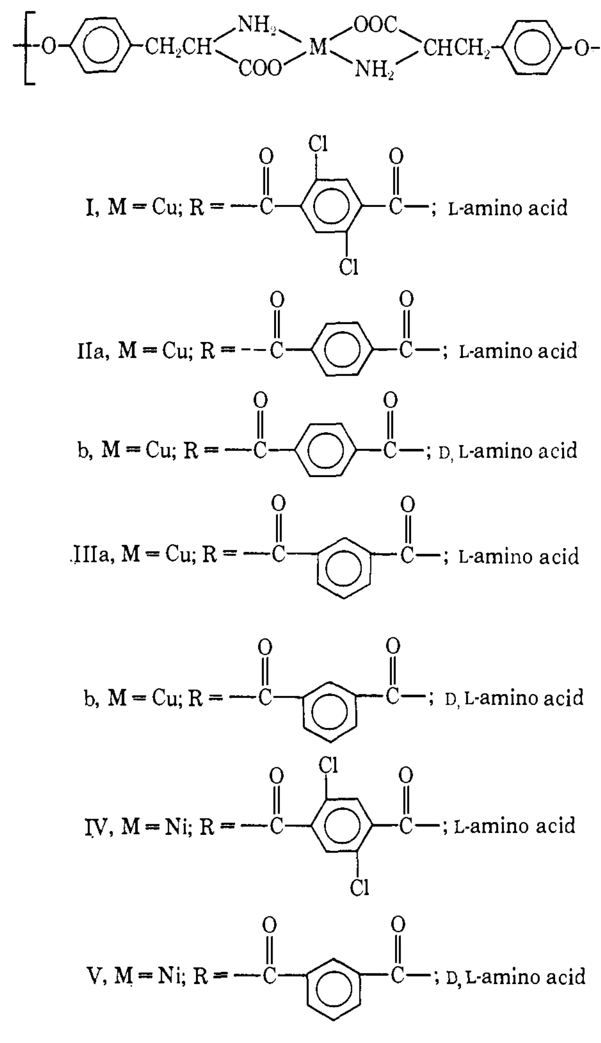

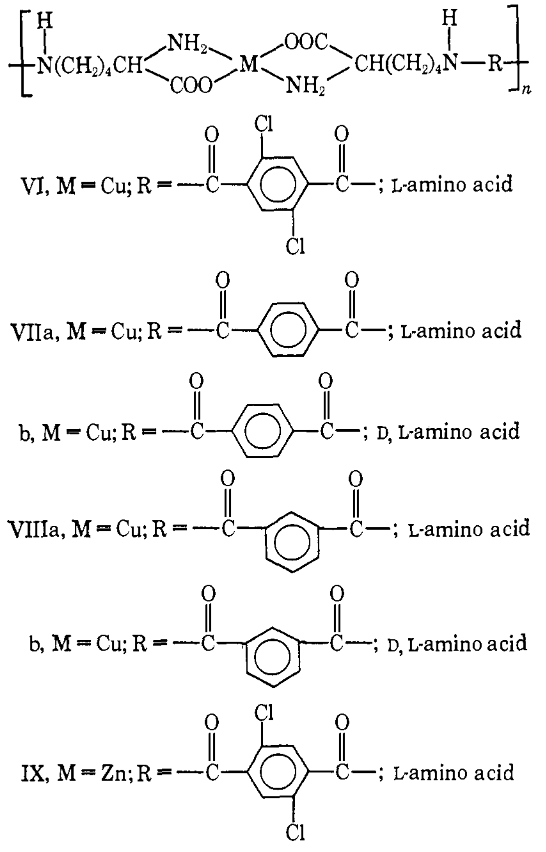

Experimental Section

Preparation of Complexes. Bis(L-tyrosinato)copper(II). This complex was prepared in 82% yield by the method of Pfeiffer and Christeleit.[8]

Anal. Calcd for $C_{18}H_{20}N_2O_6Cu$: C, 51.00; H, 4.76; N, 6.61. Cu, 14.99. Found: C, 50.98; H, 4.79; N, 6.77; Cu, 15.07.

Bis(DL-tyrosinato)copper(II). A solution of cupric acetate in a minimum amount of methanol was added to a suspension of a stoichiometric amount of DL-tyrosine in methanol. After stirring for 12–18 hr, the solution was filtered; the violet precipitate was washed with methanol and dried at 110°, yield 95%. This complex appears to have the *cis* structure.[9]

Anal. Calcd for $C_{18}H_{20}N_2O_6Cu$: C, 51.00; H, 4.76; M, 6.61. Found: C, 50.90; H, 4.52; N, 6.47.

Bis(O-benzoyl-DL-tyrosinato)copper(II) Dihydrate. This complex was prepared by the interfacial polymerization technique described below. In this case a solution of 1.406 g of benzoyl chloride in 15 ml of benzene was added to a rapidly stirred solution of 2.119 g of bis(DL-tyrosinato)copper(II), 0.40 g of sodium hydroxide, and several crystals of tetramethylammonium bromide in about 25 ml of water. A blue precipitate formed almost immediately, but stirring was continued for 10 min. The precipitate was collected and washed with benzene, water, acetone, and ethyl acetate.

Anal. Calcd for $C_{32}H_{32}N_2O_{10}Cu$: C, 57.52; H, 4.83; N, 4.19. Found: C, 57.08; H, 4.47; N, 4.18.

Bis(L-tyrosinato)nickel(II) Trihydrate. This complex was prepared in 71% yield by the method of Pfeiffer and Christeleit[8] who reported that the complex contains 2.5 water molecules. However, several different samples prepared in the course of this investigation gave the correct analysis for the trihydrate.

Anal. Calcd for $C_{18}H_{26}N_2O_9Ni$: C, 45.70; H, 5.54; N, 5.92; Ni, 12.40. Found: C, 45.70; H, 5.53; N, 6.15; Ni, 12.39.

When the light blue $Ni(L\text{-}tyr)_2 \cdot 3H_2O$ is dried to constant weight at 110°, the pale green $Ni(L\text{-}tyr)_2$ is obtained.

Anal. Calcd for $C_{18}H_{20}N_2O_6Ni$: C, 51.59; H, 4.81; N, 6.68; Ni, 14.01. Found: C, 51.17; H, 5.01; N, 6.51; Ni, 14.10.

Bis(D,L-tyrosinato)nickel(II) Dihydrate. A suspension of 7.25 g of D,L-tyrosine in 400 ml of a mixture of equal volumes of ethanol and water containing 1.60 g sodium hydroxide was added to a solution of 4.98 g of nickel acetate tetrahydrate dissolved in a minimum amount of water. The mixture was stirred for about 4 hr. The light blue precipitate which formed was filtered and washed with water and then with acetone. It was dried at 110°; yield 7.57 g (83%).

Anal. Calcd for $C_{18}H_{24}N_2O_8Ni$: C, 47.50; H, 5.32; N, 6.16. Found: C, 48.10; H, 5.40; N, 6.09.

Bis(L-lysine)copper(II) Dichloride Dihydrate. The method described by Taurins[10] was used for the preparation of this complex except that commercially prepared (Fischer Certified Reagent) basic cupric carbonate was used instead of freshly prepared cupric carbonate. The complex decomposes without melting at 205°.

Anal. Calcd for $C_{12}H_{32}Cl_2N_4O_6Cu$: C, 31.14; H, 6.97; Cl, 15.32; N, 12.10; Cu, 13.73. Found: C, 30.73; H, 6.72; Cl, 16.97; N, 12.14; Cu, 13.87.

Bis(D,L-lysine)copper(II) Dichloride. This complex was prepared in 82% yield by the method used for the preparation of $[Cu(L\text{-}lysH)_2]Cl_2 \cdot 2H_2O$. It decomposes without melting at 206°.

Anal. Calcd for $C_{12}H_{28}Cl_2N_4O_4Cu$: C, 33.77; H, 6.61; N, 13.13; Cu, 14.89. Found: C, 32.26; H, 6.65; N, 12.45; Cu, 14.03.

Bis(L-lysine)zinc(II) Dichloride Dihydrate. To a solution of 3.65 g of L-lysine hydrochloride in 75 ml of water was added a solution of 1.36 g of zinc chloride in 20 ml of water and 20 ml of 1 *N* sodium hydroxide. The precipitate of zinc hydroxide that appeared was redissolved by the addition of concentrated hydrochloric acid and the solution was slowly concentrated on a hot plate to 50 ml. It was then diluted with 100 ml of absolute ethanol and chilled to yield white needlelike crystals. The crystals were washed with absolute ethanol and then with ether; yield 2.82 g (60%).

Anal. Calcd for $C_{12}H_{32}Cl_2N_4O_6Zn$: C, 31.02; H, 7.16; Cl, 15.26; N, 12.06; Zn, 14.07. Found: C, 31.12; H, 6.87; Cl, 15.78; N, 12.07; Zn, 13.99.

Diacid Chlorides. 2,5-Dichloroterephthaloyl Dichloride. The method for the preparation of 4,6-dibromoterephthaloyl dichloride given by Chardonnens and Schmitz[11] was used; yield 87%.

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Terephthaloyl dichloride (Eastman Organic Chemicals) and isophthaloyl dichloride (Aldrich Chemical Co.) were recrystallized from petroleum ether (bp 37–47°) before use.

Preparation of Polymers. The polyamides and polyesters were prepared by interfacial polymerization in a 100-ml three-necked round-bottomed flask fitted with a cone drive stirring motor set at 1200 rpm.

Esterification. A solution of 0.005 mole of sodium hydroxide in 10 ml of water was added to a suspension of 0.0025 mole of bis(tyrosinato)metal(II) complex in 10 ml of water. A few crystals of tetramethylammonium chloride were added as a catalyst.[12] The diacid chloride (0.0025 mole) dissolved in 10–15 ml of chloroform was added, all at once, to the rapidly stirred basic solution. A precipitate formed almost immediately but stirring was continued for 15–25 minutes at room temperature. The polymer was collected, washed with water, acetone, and ether, and then extracted overnight with 95% ethanol in a Soxhlet extractor. The polymer was dried to constant weight at 110° before it was submitted for elemental analysis.

Amidation. The amidation procedure is the same as the esterification procedure except that a solution of 0.01 mole of sodium hydroxide in 10 ml of water was added to a solution of 0.0025 mole of the bis(lysine)–metal(II) dichloride complex in 10 ml of water.

Solution Polymerization. One polyamide was prepared by the following solution technique: a solution of 0.1705 g of $CuCl_2 \cdot 2H_2O$ in 5 ml of water was added, all at once, to an ice-cold, rapidly stirred solution of 2 ml of 1 *N* sodium hydroxide solution and 0.4914 g of ε-N,ε-N′-2,5-dichloroterephthaloyl dilysine in 10 ml of water. A light blue precipitate formed immediately, but stirring was continued for 15 minutes. The polymer was collected and washed with water, acetone, and ether. It was dried to constant weight at 110°.

Anal. Calcd for $[C_{20}H_{26}Cl_2N_4O_6Cu]_n$: C, 43.45; H, 4.74; Cl, 12.82; N, 10.13; Cu, 11.49. Found: C, 41.80; H, 5.01; Cl, 13.81; N, 9.98; Cu, 11.54.

Degradation of Polymers. Acidic degradation can be used for polyesters and polyamides, but basic degradation can be used only for polyamides.

Acidic Degradation of Polyesters. Concentrated hydrochloric acid was added dropwise to a stirred suspension of polyester in water in an ice bath until the insoluble blue polymer was replaced by light yellow precipitate. Hydrogen chloride gas was then bubbled into the mixture until the solution was light yellow-green. The insoluble dihydrochloride of the diester was collected in a weighed funnel, washed with dilute HCl, acetone, and ether, and then dried at 110° before it was weighed and analyzed. The following diester dihydrochlorides were obtained: O,O′-2,5-dichloroterephthaloyl dityrosine dihydrochloride hydrate, 205° dec.

Anal. Calcd for $C_{26}H_{26}Cl_4N_2O_9$: C, 47.87; H, 4.00; Cl, 21.74; N, 4.29. Found: C, 47.69; H, 3.92; Cl, 21.67; N, 4.28.

O,O′-Terephthaloyl dityrosinedihydrochloride hydrate, 210° dec.

Anal. Calcd for $C_{26}H_{28}Cl_2N_2O_9$: C, 53.52; H, 4.84; Cl, 12.15; N, 4.80. Found: C, 54.95; H, 4.77; Cl, 12.05; N, 4.96.

The pH of the filtrate was adjusted to 5–6 and hydrogen sulfide was bubbled into the solution to precipitate the metal sulfide. After removal of the metal sulfide, the pH was again adjusted to 5–6 and the solution was left standing overnight. The precipitated L-tyrosine was collected in a weighed funnel, and washed with water, acetone, and ether. It was dried in the oven and then weighed. Tyrosine was identified by its infrared spectrum.

Acidic Degradation of Polyamides. Concentrated hydrochloric acid was added dropwise to a stirred suspension of polyamide in water in an ice bath until the blue color of the polymer was gone. Then HCl gas was bubbled into the solution until the precipitate dissolved. Metal ion was then removed by treatment with hydrogen sulfide. After filtration, the solution was kept cold while it was neutralized with sodium hydroxide. The precipitated bis(L-lysine)amide was collected in a weighed funnel and dried at 110° before it was weighed and analyzed. The filtrate was treated as a solution of lysine and the procedure for isolating lysine hydrochloride described by Greenstein and Winitz[13] was used. However, the ir spectrum of the isolated compound matched that of the bis(L-lysine) amide. There was no evidence for the presence of L-lysine hydrochloride.

Basic Degradation of Polyamides. Sodium hydroxide (5 *N*) was added dropwise to a stirred suspension of the polyamide in water in an ice bath until all of the polymer had decomposed and the metal hydroxide had precipitated. The solution was filtered and H_2S was bubbled in to remove any remaining metal ion. Neutralization of the solution with concentrated HCl gave the bis(L-lysine)-amide.

The following bis(L-lysine amides were obtained: ε-N,ε-N′-2,5-dichloroterephthaloyl dilysine, 255° dec.

Anal. Calcd for $C_{20}H_{28}Cl_2N_4O_6$: C, 48.89; H, 5.75; Cl, 14.43; N, 11.40. Found: C, 48.17; H, 5.88; Cl, 15.63; N, 10.95.

ε-N,ε-N′-Terephthaloyl dilysine hydrate, 230° dec.

Anal. Calcd for $C_{20}H_{32}N_4O_7$: C, 54.53; H, 7.32; N, 12.72. Found: C, 54.91; H, 7.18; N, 12.73.

ε-N,ε-N′-Isophthaloyl dilysine hydrate, 232° dec.

Anal. Calcd for $C_{20}H_{32}N_4O_7$: C, 54.53; H, 7.32; N, 12.72. Found: C, 55.06; H, 7.08; N, 12.26.

Instrumentation and Analyses. All of the infrared spectra recorded here are those of Nujol mulls between sodium chloride or potassium bromide plates. Perkin-Elmer Model 137, Model 137G, and Model 621 spectrophotometers were used.

Melting and decomposition points were determined on a Fischer-Johns melting stage.

Thermogravimetric analyses (TGA) of one polymer and two complexes were obtained using an automatic recording thermobalance built according to the specifications of Groot and Troutner.[14]

Elemental analyses were carried out by Mr. J. Nemeth and his staff at the University of Illinois Microanalytical Laboratory.

Results and Discussion

Interfacial polymerization[15] reactions were carried out on copper, nickel, and zinc complexes of tyrosine and lysine. These complexes have the necessary "free" functional groups to undergo polymerization with diacid chlorides to form polymers I to IX (Tables I and II). Aromatic diacid chlorides were used because of their low rate of hydrolysis compared to that of aliphatic diacid chlorides.[16]

Evidence for polymer formation was provided by elemental analysis (Tables I and II), infrared spectra (Tables III and IV), and degradation studies.

The chelate polyesters and polyamides prepared in this study are insoluble in all common organic solvents and water and are decomposed by acids and bases, which cause dissociation of the metal–chelate bonds. In addition, the polyesters are saponified by dilute aqueous base.

The infrared spectra of the polyesters all have the characteristic ester carbonyl stretch around 1740 cm^{-1}. The two carbonyl stretching frequencies observed in the spectra of I and IV can be attributed to differences in site symmetry in the solid state imposed by the *ortho* halogens of the phenyl ring.[17] The carbonyl stretching frequency, amide I band in the polyamides, cannot be assigned because of the presence of several unresolved bands in the carbonyl stretching frequency region between 1670 and 1590 cm^{-1}. These unresolved bands are due to the secondary amide carbonyl group and the coordinated amino acid carbonyl group.

The thermal stabilities of the polymers are not exceptional. Most of the polymers begin to decompose be-

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Table I. Polyesters

Poly-ester	Color	Dec pt, °C	% yield^{a}	Analyses: % C Calcd^{b}	% C Found	% H Calcd^{b}	% H Found	% N Calcd^{b}	% N Found	% Cl Calcd^{b}	% Cl Found	% M Calcd^{b}	% M Found
I	Lt. blue	195	78	50.25	48.68^{c} 48.37 49.20	3.24	3.50^{c} 3.41 3.53	4.50	4.57^{c} 4.22 4.52	11.38	13.13^{c} 12.24 11.58	10.20	10.33^{c} 9.86 10.27
IIa	Lt. blue	205	90	54.77^{d}	54.45	4.28^{d}	4.37	4.90^{d}	4.91	0.00^{d}	1.32	11.11^{d}	11.23
IIb	Lt. blue	192	73	54.77^{d}	54.03	4.28^{d}	4.25	4.90^{d}	4.98			11.11^{d}	11.02
IIIa	Lt. blue	200	76	56.37	55.04	4.00	4.22	5.06	4.87	0.00	0.80	11.47	11.66
IIIb	Lt. blue	204^{f}	85	52.93^{e}	51.57	4.44^{e}	4.64	4.75^{e}	4.57			10.77^{e}	10.89
IV	Lt. green	230	89	50.53^{e}	46.81	3.26^{e}	3.57	4.53^{e}	4.49	11.47^{e}	12.63	9.50^{e}	9.05
	Lt. green	240^{f}	61^{g}	53.36^{e}	52.80	4.48^{e}	4.65	4.79^{e}	5.17			10.03^{e}	10.56

[a] Based on infinite polymer, after extraction. [b] Calculated for infinite polymer. [c] Mixture of five preparations. [d] Calculated for infinite polymer with H_2O–M. [e] Calculated for infinite polymer with $2H_2O$–M. [f] From TGA. [g] Catalyst omitted.

Table II. Polyamides

Poly-amide	Color	Dec pt, °C	% yield^{a}	Analyses: % C Calcd^{b}	% C Found	% H Calcd^{b}	% H Found	% N Calcd^{b}	% N Found	% Cl Calcd^{b}	% Cl Found	% M Calcd^{b}	% M Found
VI	Lt. blue	210	92	43.45^{c}	43.13	4.74^{c}	4.97	10.13^{c}	9.33	12.82^{c}	13.82	11.49^{c}	10.91
VI^{d}	Lt. blue	180	92		41.80		5.01		9.98		13.81		11.54
VIIa	Lt. blue	190	89	49.64	48.65	5.84	6.56	11.58	11.59	0.00	0.90	13.13	11.31
VIIb	Lt. blue	175	52^{f}	46.19^{e}	44.90	6.18^{e}	6.25	10.75^{e}	11.26			12.22^{e}	11.78
VIIIa	Lt. blue	200	80	46.19^{e}	46.98	6.18^{e}	6.06	10.75^{e}	10.71	0.00^{e}	1.60	12.22^{e}	11.73
VIIIb	Lt. blue	195	50^{f}	46.19^{e}	47.68	6.18^{e}	6.18	10.75^{e}	10.41			12.22^{e}	11.49
IX	Lt. yellow	230	80	43.31	42.24	4.72	4.71	10.10	9.81	12.78	13.42	11.78	12.16

[a] Based on infinite polymer. [b] Calculated for infinite polymer. [c] Mixture of five preparations. [d] Prepared from $CuCl_2$ and ε-N,ε-N′-2,5-dichloroterephthaloyl dilysine. [e] Calculated for infinite polymer with $2H_2O$–M. [f] Added 1/2 of calculated amount of NaOH.

Table III. Carbonyl Stretching Frequencies of Polyesters[a]

Polyester	$\nu_{C=O}$, cm^{-1}
I	1755 (s), 1740 (sh)
IIa	1735 (s)
IIb	1740 (s)
IIIa	1740 (s)
IIIb	1740 (s)
IV	1755 (s), 1740 (sh)
V	1740 (s)

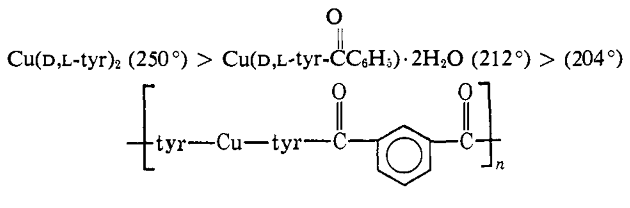
[a] Band assignments according to ref 17.

Table IV. Infrared Data of Polyamides[a]

Polyamide	ν_{N-H}	Amide II	Amide III
VI	3260 (m)	1547 (s)	1292 (m)
VIIa	3300 (m)	1534 (s)	1299 (m)
VIIb	3300, 3247 (m)		
VIIIa	3267 (m)	1536 (s)	1289 (m)
VIIIb	3290, 3247 (m)		
IX	3185 (m)		

[a] Band assignments according to ref 17.

low 200° and generally below the decomposition temperatures of the parent complexes. The thermal stability of IIIb was studied by thermogravimetric analysis and compared with the thermal stability of the parent complex and the analogous monomeric diester prepared from the complex and benzoyl chloride. The thermal stability decreases in the order



$$\mathrm{Cu(D,L\text{-}tyr)_2}\ (250°) > \mathrm{Cu(D,L\text{-}tyr\text{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{C_6H_5)\cdot 2H_2O}\ (212°) > (204°)$$

If it is assumed that the metal–ligand bond is the principal factor determining the thermal stability of the chelates, and that the presence of the electron-donating tyrosine hydroxyl group on the aromatic ring increases the strength of the metal–chelate bonds, then the presence of the carbonyl group of the diacid chloride attached to the oxygen would decrease the stability of the polyester.[7] The presence of acid chloride end groups, demonstrated by elemental analysis and a positive test with silver nitrate, may also be contributing to the instability of the polyesters.

The insolubility of the polyesters and polyamides prevents the determination of number average molecular weights by osmotic methods and end group analysis, weight average molecular weights by light scattering and ultracentrifugation, or viscosity average molecular weights by intrinsic viscosity measurements, the methods commonly used for soluble organic polymers.

Consideration of the different types of possible end groups leads to three types of polymeric units, A (two amino acid end groups), B (one amino acid, one acid chloride end group), and C (two acid chloride end groups), or A′, B′, and C′, that can be present in the ester oramide polymeric products, respectively.

Of course, B and B′ can be considered as representations of the average composition of a mixture of 50% A and 50% C and 50% A′ and 50% C′, respectively, and would be expected to be representative of the average polymer unit if both types of end groups have equal probability. This is the assumption that is generally made for purely organic polymers and is valid for very long polymer units because the end groups make such a small contribution to the total weight of a polymer unit. However, if $n < 10$, the contribution of the end groups is significant and must be considered when chelate polymers, which appear to have $n < 10$, are analyzed by de-

Table V. Data Obtained from Degradation Studies of Polyesters

Polyester	% A/ % C	$\bar{n}$	Calcd $\bar{M}_n$	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Cl Calcd	% Cl Found	% M Calcd	% M Found	Cl-M Calcd	Cl-M Found	C-M Calcd	C-M Found
I	53/47	2.8	2.4 × 10³	49.53	48.75[a]	3.28	3.48[a]	4.51	4.44[a]	12.08	12.32[a]	10.23	10.15[a]	2.28	2.17	25.8	25.0
IIa	50/50	4.5	3.2 × 10³	53.96	54.50	4.21	4.39	4.84	4.91	1.12	1.32	10.98	11.03	0.22	0.21	26.0	26.2
IIb	50/50	5	3.5 × 10³	54.02	54.03	4.21	4.25	4.84	4.98			10.99	11.02			26.0	25.9
IIIa	65/35	4	2.7 × 10³	55.59	55.04	4.02	4.22	5.09	4.87	0.83	0.80	11.56	11.66	0.17	0.12	25.6	25.0
IIIb	60/40	4	2.9 × 10³	52.20	51.57	4.46	4.64	4.76	4.57			10.79	10.89			25.7	25.0
IV	50/50	2	2.0 × 10³	46.87	46.81	3.68	3.57	4.20	4.49	12.42	12.63	8.81	9.05	2.33	2.31	26.0	25.3
V	100/0	4	2.8 × 10³	52.41	52.80	4.61	4.65	5.01	5.17			10.50	10.56			24.4	24.4

[a] Average of three preparations.

Table VI. Data Obtained from Degradation Studies of Polyamides

Polyamide	% A/ % C	% Hydrolysis of COCl	$\bar{n}$	Calcd $\bar{M}_n$	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% Cl Calcd	% Cl Found	% M Calcd	% M Found	Cl-M Calcd	Cl-M Found	C-M Calcd	C-M Found
VI	15/85	70	5	3.5 × 10³	43.21	43.13	4.61	4.97	9.65	9.33	13.83	13.82	10.93	10.91	2.25	2.27	20.9	20.9
VIIIa	13/87	31	4	2.7 × 10³	46.27	46.98	5.99	6.06	10.21	10.71	1.52	1.51	11.58	11.73	0.37	0.23	21.2	21.2

termining the amounts of the various organic compounds which are formed when the metal ion is removed. This is the method used to analyze the polymers prepared in this study.

The polymerization and decomposition reactions can be represented schematically by eq 3.

$$\mathrm{X{<}M{>}X + Y \longrightarrow [-X{<}M{>}X-Y-]_n \longrightarrow M^{2+} + X + X-Y + X-Y-X} \quad (3)$$

As n increases, the amount of X–Y–X in the product increases and the amounts of X and X–Y decrease. The amounts of X, X–Y, and X–Y–X expected for a particular value of n can be calculated readily.

Ideally one should be able to account for 100% of the polymer sample when it is decomposed, but this is not always experimentally feasible. However, the maximum amount of X–Y–X isolated gives a minimum value of n and the maximum amount of X and/or X–Y gives a maximum value of n.

The chlorine–metal ratio and the carbon–metal ratio in the polymer can be used as a further check on the average number of repeating units when they are compared with the ratios calculated for A, B, C and A′, B′, C′ as a function of n. These ratios are very sensitive to differences in end groups as a function of n when $n < 7$. Tables V and VI summarize the data obtained from the degradation studies.

The polyesters appear to have approximately equal numbers of tyrosine and acid chloride end groups. The presence of the acid chloride end groups indicates that the degree of polymerization is governed by the solubility of the polyester rather than the hydrolysis of the diacid chloride as was observed by Interrante and Bailar[7] for the polyesters of azo and azomethine complexes with sebacyl chloride and phosgene.

The lowest degree of polymerization is found for the 2,5-dichloroterephthalate esters, I and IV. 2,5-Dichloroterephthaloyl dichloride is less soluble than terephthaloyl and isophthaloyl dichloride and might be expected to yield a less soluble polyester.

The presence of only tyrosine end groups in the nickel polyester, V, is accounted for by the fact that the polymer was isolated from the reaction mixture 2 days after the reactants had been stirred together. Excess base present in the aqueous layer appears to have caused hydrolysis of any isophthalate groups attached to the polymer by only one ester linkage.

The polyamides appear to have less than 20% lysine end groups, probably because of the rapid rate of reaction of an amino group with an acid chloride. However, the remaining end groups are both acid chloride and carboxylic acid. The greater basicity of the basic aqueous lysine complex solution, in which the added hydroxide is not neutralized, over the basic tyrosine complex solution, increases the rate of hydrolysis of the acid chlorides so that at least 30% of the acid chloride end groups in the polymer have hydrolyzed. The partial hydrolysis of acid chloride end groups adds an extra complication to the determination of polymer length. However, the degree of polymerization appears to be the same as for polyesters.

The necessity of adding a strong base, such as sodium hydroxide, to the aqueous phase limits the applicability of the interfacial polymerization technique to chelate polymerizations of complexes which are not dissociated in the basic aqueous phase prior to polymerization.

Table VII. Infrared Data for Dilysine Diamides[a]

Compound	ν_{N-H}	$\nu_{NH_3^+}$	Amide I, $\nu_{C=O}$	COOH, $\nu_{C=O}$	NH_3^+ DEF	Amide II N-H DEF	Amide III	⌬ ring C-H bend
XII	3250 (m)	3060 (m sh)	1658 (s) 1652 (s)	1605 (s sh)	1586 (s)	1555 (s)	1308 (m)	895 (m)[b]
XIII	3315 (m)	3060 (m sh)	1634 (s)	1605 (s sh)	1585 (s)	1547 (s)	1290 (m)	860 (m)[c]
XIV	3305 (m) 3260 (m)	3060 (m sh)	1638 (s)		1582 (s)	1535 (s)	1296 (m)	

[a] Band assignments according to ref 17. [b] 1,2,4,5-benzene ring substitution. [c] 1,4-benzene ring substitution.

Thus the polyamidation of bis(L-lysine)zinc(II) dichloride dihydrate yielded a product containing zinc hydroxide because of partial dissociation of the complex in the basic aqueous phase.

The removal of the metal ion from the polyesters and polyamides yielded six new organic compounds, O,O′-2,5-dichloroterephthaloyl dityrosine, O,O′-terephthaloyl dityrosine, O,O′-isophthaloyl dityrosine, ε-N,ε-N′-2,5-dichloroterephthaloyl dilysine (XII), ε-N,ε-N′-terephthaloyl dilysine (XIII), and ε-N,ε-N′-isophthaloyl dilysine (XIV), which could not have been readily prepared by other methods.

The dityrosine diesters have the ester carbonyl stretching frequency around 1740 cm^{-1}. The significant infrared stretching frequencies of the dilysine diamides are summarized in Table VII.

In this study it was found that the degree of polymerization is primarily governed by the insolubility of the products formed. This appears to be due primarily to the localized charge distribution about the metal ions. Therefore, complexes containing more highly covalent bonds should form polymers of higher molecular weight.

To date no methods for the determination of molecular weights or the degree of polymerization of insoluble chelate polymers have been reported. However, the method described above should be applicable to other chelate polymers prepared by the polymerization of metal chelates containing free functional groups if the metal ion can be removed without destroying other bonds. For high molecular weight polymers this method can tell at least the minimum degree of polymerization. However, for low molecular weight polymers, in which fragments containing the end groups can be isolated, the maximum degree of polymerization can also be determined.

Acknowledgments. The authors wish to thank the Indiana University Chemistry Department for the loan of laboratory space to Ieva O. Hartwell and Dr. George E. Hartwell for many helpful discussions. We also wish to thank the National Science Foundation for financial assistance through Grant G-CP-191.

Photochromic Spiropyrans. I. Absorption Spectra and Evaluation of the π-Electron Orthogonality of the Constituent Halves

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Received June 11, 1969

Abstract: The absorption transitions of a series of indolinobenzospiropyrans, at both room temperature and 77°K, for the colorless forms are presented. In addition, spectral data are given for chromenes and an indoline which are treated as models for the appropriate halves of the benzospiropyrans. Analyses of the effect of substitution on the electronic transitions of the model compounds and the benzospiropyrans show that the absorption transitions of the colorless forms are essentially localized on a particular half of the molecule. In addition, a vibrational analysis of the chromene transitions of β-naphthospiropyran is given and shown to be similar to that for dimethylbenzochromene.[2] Assignments of the nature of the absorption transitions, *i.e.*, whether of $\pi^* \leftarrow n$ or $\pi^* \leftarrow \pi$ character, are made for a number of the molecules considered.

Although a great amount of interest has been shown in the spiropyrans as photochromic substances,[3] only a few electronic emission studies and electronic state assignments have been made.[4] The photochromic trans-

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(1) Taken from a dissertation to be submitted in partial fulfillment of the requirements for the Ph.D. degree.

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(3) In a recent comprehensive photochromism and thermochromism literature survey by the authors, over 75 references were found dealing with the spiropyrans.

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