[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNION CARBIDE PLASTICS COMPANY, BOUND BROOK, NEW JERSEY]

Inner Complexes. II. Macrocyclic Beryllium Chelates and their Polymers[1]

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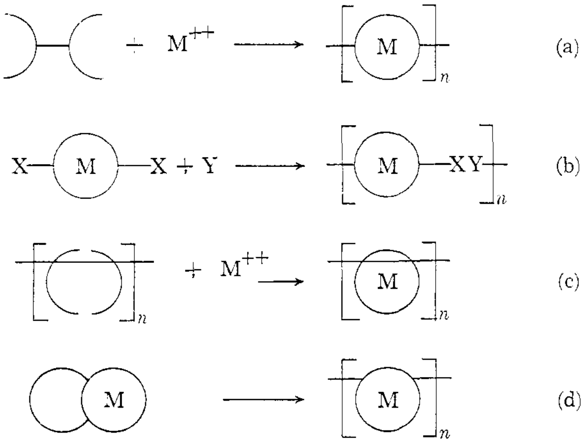
Macrocyclic β-dicarbonyl beryllium chelates have been prepared by thermal degradation of the corresponding low molecular weight polymers. These cyclic monomers and dimers polymerize upon heating above their melting points to produce high molecular weight, linear chelate polymers soluble in aromatic solvents.

The preparation of linear polymers incorporating coördinated metal atoms in the backbone has been stimulated by present technological requirements for materials of extraordinary properties. Generally chelate polymers have been prepared by three procedures shown schematically in Table I: (a) the condensation of a difunctional ligand and a metal compound[2]; (b) preparation of a metal chelate compound containing free functional groups and polymerization by conventional procedures through these functional groups[3]; (c) preparation of a polymer containing built-in ligands and subsequent chelation.[4] However, due to such factors as polymer insolubility, the competition of solvent for coordination sites, thermal degradation of monomer and/or polymer, the inability to completely remove volatile by-products and perhaps inexact stoichiometry caused by volatilization, side reactions of monomer, or impurities, none of these methods has produced polymer of proven high molecular weight. A polymerization method which eliminates many of the above problems is the addition polymerization of a cyclic monomer. This method has not previously been utilized in the formation of chelate polymers due to the unavailability of suitable cyclic monomers.

TABLE I

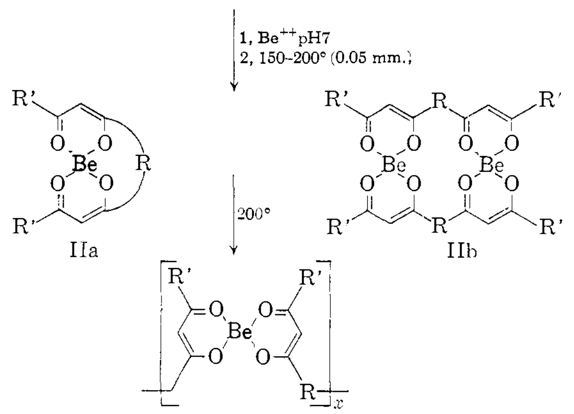
METHODS FOR CHELATE POLYMER POLYMERIZATION



Crystalline macrocyclic beryllium β-dicarbonyl chelates(II) now have been prepared by vacuum sublimation of the low polymer obtained from the interaction of a bis-β-dicarbonyl compound (I) with beryllium salts in a neutral medium. Above their melting points these macrocycles are converted to polymers shown by solution properties to be of high molecular weight. This presents a new method for the formation of coördination polymers and represents the first synthesis of truly high molecular weight linear chelate polymers.

$R'COCH_2CO—R—COCH_2COR'$

I



IIa IIb

III

Experimental

Bis-β-diketones were prepared by the method of Fernelius and Holst[5] from acetone and a diester using sodium amide. Bis-acetoacetic esters were prepared from ethyl acetoacetate and a glycol in toluene.[6] The bis-acetoacetamides were prepared by the reaction of a diamine with ketene dimer[7] (see Table IIA).

Preparation of Cyclic Monomer: Cyclic Beryllium Chelate of 2,4,13,15-Tetraketohexadecane.—2,4,13,15-Tetraketohexadecane 3.000 g. (0.0106 mole) and 1.881 g. (0.0106 mole) of beryllium sulfate tetrahydrate were stirred in a 125 ml. flask containing 50 ml. of distilled water and 10 ml. of purified dioxane. The reaction mixture was neutralized to *p*H 8 with sodium hydroxide, stirred for an additional 16 hr. and the insoluble product removed by filtration. Using solvent extraction, this material was found to contain low polymer, starting tetraketone and beryllium salts. The reduced viscosity of the benzene-soluble portion was 0.05 (0.2 g./100 ml. of benzene at 25°). Sublimation of the crude product at 200° (0.2 mm.) gave 2.3 g. (74%) of quite pure cyclic monomer, m.p. 138–140° (with polymerization).

Anal. Calcd. for $C_{16}H_{24}O_4Be$: Be, 3.1; mol. wt., 289. Found: Be, 3.0; mol. wt., 272 (by freezing point depression in benzene).

The product could be purified further by resublimation at 120° (0.05 mm.).

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[1] Presented at the 137th meeting of the American Chemical Society, April 11, 1960.

[2] J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711 (1953) (du Pont); W. C. Fernelius, W. A. D. C. Tech. Report No. 56-203; C. S. Marvel and J. H. Rassweiler, THIS JOURNAL, **80**, 1197 (1958); C. S. Marvel and M. M. Martin, *ibid.*, **80**, 6600 (1958); K. V. Martin, *ibid.*, **80**, 233 (1958); W. F. Amon and M. W. Kane, U. S. Patent 2,505,085 (1950) (Polaroid).

[3] J. C. Bailar, W. A. D. C. Tech. Report No. 57-657.

[4] C. S. Marvel and N. Tarköy, THIS JOURNAL, **79**, 6000 (1957).

[5] E. H. Holst, Doctoral Dissertation, Pennsylvania State University, August, 1955.

[6] British Patent 791,326, Feb. 26, 1958.

[7] Y. Iwakura, K. Nagakubo, Y. Matsuga and F. Liu, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 67 (1955); *C. A.*, **50**, 4008e (1956).

Other macrocyclic chelates were prepared analogously. The chelates of the bis esters normally were isolated by sublimation at 140–180° to minimize side reactions. The yields from the bis esters were in the range 20–30%. Table IIB presents analytical data on the cyclic monomers.

Preparation of the Cyclic Monomer and Dimer Chelate of 2,4,11,13-Tetraketotetradecane.—The 2,4,11,13-tetraketotetradecane (2.54 g., 0.01 mole) and 1.77 g. of beryllium sulfate tetrahydrate (0.01 mole) were stirred in 50 ml. of water and 10 ml. of dioxane for 1 hr., neutralized with sodium hydroxide to *p*H 8 and stirred at room temperature an additional 16 hr. The crude precipitate was transferred to a sublimation tube and sublimed at 200° (0.2 mm.) for two weeks. The sublimate crystallized on the sides of the tube in two zones. The lower zone (warmer area) produced 56 mg. of material, m.p. 230° (polymerizes). The upper zone (cooler area) produced 379 mg. of material which polymerized without observable melting at 110°. This upper zone corresponded to the area in which the cyclic beryllium chelate of 2,4,13,15-tetraketohexadecane condensed and by analogy and in agreement with infrared and analytical data, this material has been assigned the structure of the cyclic monomer. This was confirmed by molecular weight determinations (freezing point depression in benzene) which gave 277 (calcd. 261). The less volatile component had an infrared spectrum essentially identical with the monomer and in agreement with its analytical data and volatility has been assigned the dimer structure. Cryoscopic molecular weight determinations in benzene gave 555 (calcd. 522). The recovered dimer melted at 215 (polymerized).

Cyclic Dimer from Tetramethylene Bis-acetoacetate.—Tetramethylene bis-acetoacetate 5.2 g. (0.2 mole) and 3.6 g. (0.02 mole) of beryllium sulfate tetrahydrate were stirred in 50 ml. of water and neutralized to *p*H 8. The crude insoluble material obtained after 16 hr. was sublimed at 145–160° for ten days to produce 43 mg. of material, m.p. 180° (polymerizes). By comparison of its volatility with that of other macrocyclic chelates of bis-acetoacetic esters known to be monomers from molecular weight data, the product was assigned the structure of a dimer. Its analysis, Table IIC, and its infrared spectrum support this assignment.

Infrared Spectra.—The cyclic beryllium bis-β-diketonates both monomer and dimer pressed in KBr pellets contained a characteristic doublet at 6.35 and 6.53μ essentially identical to that found in beryllium bis-(2,4-pentanedionate), 6.34 and 6.50μ.[8] The tetraketones from which these chelates were derived absorbed as KBr films at 6.10 and 6.25μ and as solid films on NaCl plates at 5.72, 6.10 and 6.25μ. No evidence for uncoördinated carbonyl groups was found in the spectra of the macrocyclic chelates. Similarly the chelates derived from the bis-acetoacetic esters absorbed (as KBr films) at 6.25 and 6.55μ and showed no trace of free carbonyl. This is in agreement with the spectrum of the beryllium chelate of ethyl acetoacetate which absorbs at 6.23 and 6.62μ. The amide chelates absorbed at about 6.30μ and 6.55μ in agreement with a model compound, the beryllium chelate of N,*n*-butylacetoacetamide, m.p. 167–168°, absorbing at 6.31 and 6.55μ.

Anal. Calcd. for $C_{16}H_{28}N_2O_4Be$: C, 59.79; H, 8.78; N, 8.71. Found: C, 59.96; H, 8.96; N, 8.69.

The parent bis-acetoacetamides absorbed at 5.77, 6.05 and 6.36μ. No trace of these absorptions was found in the chelate spectra. The N-H stretching frequencies at approximately 3.05 and 3.20μ were duplicated in both the chelates and unchelated amide, confirming the anticipated Be–O bonding.

Polymerization of Macrocycles.—Upon heating above their melting points these crystalline macrocycles spontaneously polymerized producing amorphous (by X-ray) materials which dissolved slowly in benzene. These polymers have intrinsic viscosities in the range 0.1–2.7 characteristic of high molecular weight polymers. This characterization of high molecular weight was confirmed by the mechanical properties of several of these materials. As example, the polymer III, R' = CH_3, R = $(CH_2)_8$, intrinsic viscosity 0.9, was flexible at room temperature (glass transition temperature 35°) and had a tensile modulus at 25° of 122,000 p.s.i. and a tensile strength (100% elongation/min.) of 2710 p.s.i. Melt index flow rates at 190° (ASTM Test D 1238-52T) were in the range 0.1–2.0 decigrams/min., again characteristic of high molecular weight polymer. The analytical and infrared data on these polymers were in agreement with the assigned structures.

Thermal Degradation of Polymers III *in vacuo*.—Cyclic monomer IIa (950 mg.) was placed in a shell vial (diameter 7.5 mm.) and heated at 200° (atmospheric pressure) for fifteen minutes to effect polymerization. In order to insure constant surface volume, the cyclic monomer always was placed carefully in the bottom of the vials and the vials always heated in a vertical position. Traces of polymer which formed on the sides of the vials were removed by sublimation at 200° (0.1 mm.) for fifteen minutes. After this initial heating period, the vials were heated in a sublimation tube at 205 ± 2° for periods of sixty minutes and the weight losses recorded. The rates of degradation of the polymers III R = $(-CH_2)_n$ to cyclic monomers II decreased in the order $n = 10$, $n = 12$, 10 mg./hr.; $n = 8$, 9 mg./hr.; $n = 7$, 4.5 mg./hr.; $n = 6$, <1 mg./hr. The rate was essentially constant over the first 3 hr. Smaller quantities of polymer (10–20 mg.) produced somewhat slower rates of degradation. The intrinsic viscosities of all of the above polymers were in the range 0.8–1.2.

TABLE II

R	M.p., °C.	Carbon, %[a]		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
(A) Bis-β-dicarbonyl ligands (I, R' = CH_3)					
$(CH_2)_6$	69.0–69.5	66.11	65.85	8.72	8.58
$(CH_2)_7$	72.5–73.5	67.13	67.18	9.01	8.89
$(CH_2)_8$	77.8–78.5[b]	68.05	68.05	9.28	9.13
$(CH_2)_{10}$	83.2–84.0	69.64	69.83	9.74	9.77
$(CH_2)_{12}$	88.0–89.0	70.97	71.06	10.12	9.99
$NH(CH_2)_6NH$	150–150.5[c]	59.13	59.69	8.51	8.52
$NH(CH_2)_{10}NH$	152–152.5	63.50	63.70	9.47	9.46
p-$(O(CH_2)_2O)_2C_6H_4$	87–88	59.01	58.43	5.42	5.77
$O(CH_2)_6O$[d]	36–39	42.64	43.47	4.09	4.32
(B) Cyclic monomer (IIa, R' = CH_3)					
$(CH_2)_6$	*ca.* 110	64.34	63.65	7.71	7.82
$(CH_2)_7$	132–135	65.43	66.02	8.06	7.70
$(CH_2)_8$	139–140.5	66.41	66.71	8.36	8.66
$(CH_2)_{10}$	139–140	68.11	68.43	8.89	9.12
$(CH_2)_{12}$	141.5–143	69.53	69.86	9.34	9.41
$NH(CH_2)_6NH$	246–249	57.51	58.78	7.59	7.54
$NH(CH_2)_{10}NH$	243–245	62.22	62.67	8.70	8.17
$O(CH_2)_6O$	139–141	57.32	57.64	6.87	6.74
$O(CH_2)_{10}O$	87–89	61.87	62.21	8.08	8.31
$O(CH_2CH_2O)_2$	166–168	51.69	51.49	6.20	6.62
p-$(OCH_2CH_2O)_2$-C_6H_4	176–178	57.90	57.87	5.39	5.53
$O(CH_2)_6O$[d]	96–100	41.90	42.34	3.52	3.80
(C) Cyclic dimers (IIb, R' = CH_3)					
$(CH_2)_6$	230	64.34	64.31	7.71	7.54
$O(CH_2)_4O$	180	55.27	54.70	6.19	6.63

[a] Analyses by Weiler and Strauss, Oxford, England. [b] Reported 78–80°.[6] [c] Reported 145.5–146.0°.[8] [d] R' is CF_3.

Discussion

Macrocyclic copper chelates are reported to be formed by direct interaction of copper salts with a difunctional ligand.[9] However, no evidence for the formation of macrocycles involving beryllium and difunctional ligand has been presented, the principal products of such interactions being amorphous, low molecular weight polymers. Crystalline macrocyclic beryllium chelates have now been obtained by the thermal degradation *in vacuo* of the low chelate polymers formed from bis-β-dicarbonyl compounds. Monomeric products are isolated when R is a polymethylene chain of six units or greater or either an α,ω-dioxypolymethylene or a α,ω-diiminopolymethylene group of at

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(8) H. F. Holtzclaw, Jr., and J. P. Collman, THIS JOURNAL, **79**, 3318 (1957); L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 126.

(9) N. Schlesinger, *Ber.*, **58**, 1877 (1925); M. Calvin and C. H. Barkelew, THIS JOURNAL, **68**, 2267 (1946); P. Pfeiffer and H. Pfitzner, *J. prakt. Chem.*, (2) **145**, 243 (1936); P. Pfeiffer, E. Breith, E. Lubbe and T. Tsumaki, *Ann.*, **503**, 84 (1933).

least six methylene units. Chelates having shorter links tend to form dimers; however, the shorter the link, the less readily are volatile products formed. Phenylene and/or ether linkages can be substituted for some of the methylene groups. The cyclic structure was confirmed by the volatility of the products, elemental analysis, infrared spectra and molecular weight determinations.

Polymer degradation to macrocyclic products was studied using the bis-β-diketone system (II and III R = $-(CH_2)_n$), which, unlike the ester and amide derivatives, could be polymerized and depolymerized quantitatively at 200°. (The ester and amide chelates became highly cross-linked upon prolonged heating, preventing very good recovery of cyclic monomer.) At a constant surface area, pressure and temperature, the rate of macrocycle formation was approximately constant. In the series studied, this rate decreased in the order n = 12, n = 10, 10 mg./hr.; n = 8, 9 mg./hr.; n = 7, 4.5 mg./hr.; n = 6 < mg./hr. (205°, 0.05 mm.). This order is that expected by the increasing strain incorporated in the macrocycles with decreasing chain length and roughly parallels literature data on the thermal degradation of polyesters, poly-anhydrides and polylactones.[10] Further qualitative data on the amount of strain incorporated in these macrocycles was evidenced by their rate of polymerization in the melt. The compound IIa (R = $-(CH_2)_6$) polymerized instantly upon melting at about 110°, no low viscosity stage being discernible; whereas IIa R = $-(CH_2)_{10}$ could be recovered partially even after heating one minute in the melt at 140°.

Under conditions of macrocycle formation the polymer and the macrocycles are in equilibrium. Removal of the volatile components results in an increase in molecular weight of the residual polymer suggesting that the more volatile components of the polymer include chain stopping end groups. Because of the re-equilibration of polymer and macrocycles during degradation, it is difficult to determine whether cycle formation proceeds by unzippering with concurrent repolymerization of monomers or involves random chain cleavage as well. However, attempts to stabilize the polymer against unzippering by mixing 10% of the hexamethylene monomer IIa (R = $-(CH_2)_6-$ with octamethylene monomer IIa R = $-(CH_2)_8-$ to produce what is believed to be a copolymer gave polymer which degraded at essentially the same rate as the pure octamethylene polymer III (R = $-(CH_2)_8-$). Likewise, partial crosslinking of the octamethylene polymer by irradiation failed to decrease the rate of macrocycle formation appreciably. These results suggest that, although unzippering may be the principal mode of cycle formation, random chain cleavage and re-equilibration of chains must also be important.

The rate of polymerization in the melt of cyclic chelates derived from a diester (*e.g.*, IIa R = $-O(CH_2)_6O-$) was qualitatively observed to be much faster than for the corresponding diketone chelate containing an equal number of links in the macrocycle (*e.g.*, IIa R = $-(CH_2)_8-$). This is contrary to the expected behavior based on strain if only such factors as hydrogen crowding were involved. This suggests that the oxygen atoms prefer to orient coplanar to the ring and participate in resonance stabilization.[11] The geometry of the ring prohibits this except at the expense of additional strain. Thus, the energy content of the monomer relative to the polymer is raised and accounts for the faster polymerization rate. This postulate is in agreement with the observation that both IIa and IIb (R = $-(CH_2)_6-$) can be isolated whereas only the dimer IIb (R = $O(CH_2)_4O$) can be isolated. This postulates also further correlates with the glass transition temperatures of the resulting polymers, a measure of the rigidity of the components of a polymer. The glass transition temperature of the polymer III R = $-O(CH_2)_6O-$ (approximately 55°) corresponds to that of III R = $-(CH_2)_6-$ rather than III R = $-(CH_2)_8-$ (35°), again suggesting that the oxygens adjacent to the chelate ring do not rotate freely as do adjacent methylene groups.

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[10] E. W. Spanagel and W. H. Carothers, This Journal, **57**, 929 (1935); M. Stoll and A. Rouve, *Helv. Chim. Acta*, **18**, 1087 (1935), K. Ziegler and H. Holl, *Ann.*, **528**, 143 (1937).

[11] R. J. B. Marsdon and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936); M. Calvin and K. W. Wilson, This Journal, **67**, 2003 (1945).

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Unusual Proton Affinities of Some Mixed Ligand Iron(II) Complexes

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The neutral dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2′-bipyridine)-iron(II) complexes have been found to react reversibly with acid and to exhibit appreciable dibasic character. Properties of the complexes and their protonated species have been investigated and are interpreted to rationalize how and where protonation takes place.

Evidence was reported in a previous paper[1] concerning the existence of stable protonated species of the neutral mixed ligand complexes: dicyano-bis-(1,10-phenanthroline)-iron(II) and dicyano-bis-(2,2′-bipyridine)-iron(II). That these complexes react reversibly with protons is most surprising. Certainly it seems unreasonable to expect a ligand as weakly basic as the aromatic diimines in question to retain any significant proton affinity following metal ion coördination. The more strongly basic cyanide ligands might more conceivably have some residual proton affinity: however the coördination properties of hydrogen

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[1] A. A. Schilt, This Journal, **82**, 3000 (1960).