The Complexes of Pyridinaldazine with Iron(II) and Nickel(II)

BY WILMER J. STRATTON AND DARYLE H. BUSCH

Complex compounds of iron(II) and nickel(II) with 2-pyridinaldazine (PAA) have been prepared and characterized as the iodide, perchlorate and fluoborate salts. An unusual behavior is observed with this ligand. The expected compounds, $[M(PAA)_2]X_2$, in which two of the donor molecules coördinate in a tridentate manner with a single metal ion, can be prepared. In addition, a second type of compound has been isolated, in which the composition is $M_2(PAA)_3X_4$. For the latter type, evidence is presented in support of a dinuclear cation in which each ligand molecule appears to act as a bidentate ligand toward each of two metal ions. Conductivities of 10^{-3} molar solutions have been measured and are consistent with electrolytes of the types $[M(PAA)_2]X_2$ and $[M_2(PAA)_3]X_4$. Magnetic susceptibility measurements are in agreement with these formulations.

Introduction

Complexes of iron(II) and nickel(II) have been prepared with a variety of tridentate chelating agents. Among the best known compounds of this type are the 2,2′,2″-terpyridine (I) derivatives,[1] in which two ligand molecules coördinate with each metal ion, forming octahedral complexes. The iron(II) derivative of this ligand is diamagnetic, while the nickel derivative is paramagnetic. A closely related ligand is 8-(α-pyridylmethyleneamino)-quinoline (II), which forms a similar compound with iron(II).[2] In the latter case, the iron(II) compound has been resolved into optical isomers, which exist because of the unsymmetrical nature of the ligand. In order

I   II
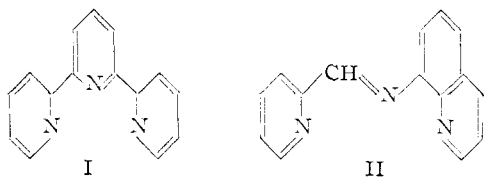
that these ligands preserve their coplanarity, the expected stable configuration should be the one in which each molecule coördinates along an edge of the octahedron formed about the metal ion. Recent work in this Laboratory has shown that 2,6-pyridindialdihydrazone (III) likewise behaves as a tridentate toward nickel(II) and iron(II) in a manner similar to I and II.[3] Other compounds, related to structure III by replacement of the NH_2 groups with other substituents, have more recently been reported.[4]

An additional ligand of this type, 2-pyridinaldazine (IV), is reported here.

III

IV
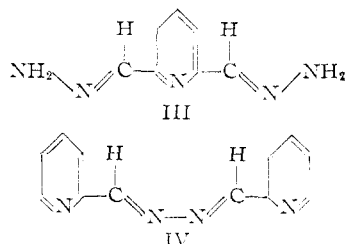
This compound might be expected to behave as a

(1) G. T. Morgan and F. H. Burstall, J. Chem. Soc., 1649 (1937); W. Brandt, F. Dwyer and E. Gyarfas, Chem. Revs., 54, 412 (1954).

(2) F. Dwyer, N. Gill, E. Gyarfas and F. Lions, THIS JOURNAL, 75, 3834 (1953).

(3) R. C. Stoufer and D. H. Busch, ibid., 78, 6016 (1956).

(4) F. Lions and K. V. Martin, ibid., 79, 2733 (1957).

tridentate chelating agent, in which either of the two azine nitrogens might coördinate, along with the two pyridine nitrogens. Pyridinaldazine (P-AA) would also be expected to be coplanar because of its high degree of conjugation, and therefore should coördinate along an edge in a manner analogous to that of the previously mentioned tridentates. There is, however, a difference in the chelate rings it might form. Whereas I and II form two five-membered rings with a metal atom, PAA should form one five-membered ring and one six-membered ring. It is to be noted that the necessary conditions are provided for asymmetry in the two-to-one compounds and that these octahedral complexes should be susceptible to resolution.

A second striking difference between pyridinaldazine and terpyridine is also of significance. The presence of four nitrogen atoms in the case of PAA presents the possibility of coördination in a tetrafunctional manner. The location of the two azine nitrogens adjacent to each other renders unlikely the coördination of all four donor atoms to a single metal ion. It probably would be necessary for this molecule to combine with at least two metal ions in order to utilize all four nitrogen atoms.

The investigations reported here have revealed that pyridinaldazine forms two types of compounds. One type involves the expected octahedral complexes containing two moles of the ligand acting as a tridentate group. These compounds are of the general formula $[M(PAA)_2]X_2$. The second type of compound has the unusual stoichiometry represented by the formula $M_2(PAA)_3X_4$. Both series of compounds have been isolated in pure form as iodide, perchlorate and fluoroborate salts. The perchlorate salts were prepared in order to have a non-coördinating anion, but because of the explosive nature of the perchlorates and the attendant difficulties in analysis, the fluoroborate salts also were prepared. The authors wish to point out that fluoroborate salts of metal complexes are fully as satisfactory, for many purposes, as perchlorate salts. The compounds have been characterized further by magnetic measurements and conductivity studies. Evidence is presented in support of a dinuclear structure for the compounds containing metal ion and ligand in the ratio of two to three.

Experimental

2-Pyridinaldazine.—2-Pyridinaldazine was first prepared

by Harries and Lenart.[5] The 2-pyridinaldehyde used in the present work was obtained from the Aldrich Chemical Company and used without further purification. Twenty milliliters of anhydrous hydrazine (0.63 mole) in 200 ml. of ethanol was added slowly with stirring to a solution of 160 g. of 2-pyridinaldehyde (1.5 moles) in 200 ml. of ethanol. During the addition, the solution became quite hot and, upon continued stirring, crystals of 2-pyridinaldazine appeared. The mixture was cooled, filtered and recrystallized from approximately 350 ml. of ethanol; yield 115 g. (73%), m.p. 146–147° (lit.[5] 149°). *Anal.* Calcd. for $C_{12}H_{10}N_4$: C, 68.5; H, 4.8; N, 26.6. Found: C, 68.4, 68.4; H, 4.7, 4.9; N, 26.4, 26.6. The azine consists of yellow needles, which are insoluble in water, but easily soluble in hot ethanol.

Bis-(pyridinaldazine)-iron(II) Iodide 1-Hydrate.—Two and eight-tenths grams of iron(II) sulfate 7-hydrate (0.010 mole) was dissolved in 75 ml. of water. Four grams of pyridinaldazine (0.019 mole) was added, producing a deep red color almost instantaneously. The mixture was heated on a steam-bath for 10 minutes, during which time the color changed from an intense red to an intense blue, and was accompanied by the dissolution of nearly all the ligand. The hot solution was filtered to remove any undissolved ligand and 5 g. of potassium iodide was added. Upon cooling in an ice-bath, dark blue-black needle-shaped crystals separated. These were filtered and recrystallized from 125 ml. of hot water with 2 g. of potassium iodide added. The purified product was filtered and washed with several portions of cold absolute ethanol, followed by anhydrous ether. During the ethanol washing the color of the filtrate changed from olive-red to colorless, to pale blue. The product was dried *in vacuo* over P_2O_5 at room temperature; yield 5.1 g. *Anal.* Calcd. for $[Fe(C_{12}H_{10}N_4)_2]I_2 \cdot H_2O$: C, 38.5; H, 3.0; N, 15.0; I, 34.0; Fe, 7.5. Found: C, 38.8; H, 3.3; N, 15.0; I, 34.8; Fe, 7.7.

Bis-(pyridinaldazine)-nickel(II) Iodide 2-Hydrate.—Two and four-tenths grams of nickel(II) chloride 6-hydrate (0.10 mole) and 4 g. of pyridinaldazine (0.019 mole) were added to 50 ml. of water and the mixture was heated on a steam-bath for 10 minutes. During this time the color became deep red. The hot solution was filtered to remove any undissolved ligand and 8 g. of potassium iodide was added. Upon cooling in an ice-bath, a maroon microcrystalline product separated. This was recrystallized from 40 ml. of hot water with 2 g. of potassium iodide added. The purified product was washed with absolute ethanol and anhydrous ether and dried *in vacuo* over P_2O_5 at room temperature; yield 4.6 g. *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_4)_2]I_2 \cdot 2H_2O$: C, 37.5; H, 3.1; N, 14.6; I, 33.0; Ni, 7.6. Found: C, 37.7, 37.7; H, 3.1, 3.2; N, 14.5, 14.4; I, 32.7; Ni, 7.5.

Tris-(pyridinaldazine)-di-iron(II) Iodide 2-Hydrate.—Five and three-tenths grams of iron(II) sulfate 7-hydrate (0.019 mole) and 4 g. of pyridinaldazine (0.019 mole) were added to 100 ml. of water. The mixture was kept at room temperature and stirred mechanically for five minutes, during which time nearly all of the ligand dissolved and the solution became an intense red. The solution was filtered to remove any undissolved ligand and, upon adding a solution of 6 g. of potassium iodide in 10 ml. of water, beautiful red-black crystals quickly began to separate. After cooling in an ice-bath, the crystals were filtered, washed with ethanol and ether, and dried *in vacuo* over P_2O_5 at room temperature; yield 6.5 g. of well-formed prisms. The compound was not recrystallized because of slow conversion to the blue compound. *Anal.* Calcd. for $[Fe_2(C_{12}H_{10}N_4)_3]I_4 \cdot 2H_2O$: C, 33.6; H, 2.7; N, 13.1; I, 39.5; Fe, 8.7. Found: C, 33.6; H, 3.0; N, 13.0; I, 40.0; Fe, 9.1.

Tris-(pyridinaldazine)-di-nickel(II) Iodide 2-Hydrate.—Three and four-tenths grams of nickel(II) chloride 6-hydrate (0.014 mole) and 3 g. of pyridinaldazine (0.014 mole) were added to 75 ml. of water. The mixture was stirred mechanically for 15 minutes at room temperature and filtered to remove any undissolved ligand from the bright red solution. A solution of 10 g. of potassium iodide in 10 ml. of water was added with stirring, and glittering scarlet crystals quickly began to separate. After cooling in an ice-bath, the crystals were filtered, washed with ethanol and ether, and dried *in vacuo* over P_2O_5 at room temperature; yield 3.4 g. *Anal.* Calcd. for $[Ni_2(C_{12}H_{10}N_4)_3]I_4 \cdot 2H_2O$: C,

33.5; H, 2.7; N, 13.0; I, 39.3; Ni, 9.1. Found: C, 33.5, 33.4; H, 2.8, 2.8; N, 13.0, 12.9; I, 39.5; Ni, 9.3.

The perchlorate and fluoroborate salts listed have been prepared in the same manner as the corresponding iodide salts described above:

Bis-(pyridinaldazine)-iron(II) perchlorate 2-hydrate: dark blue crystalline powder. *Anal.* Calcd. for $[Fe(C_{12}H_{10}N_4)_2](ClO_4)_2 \cdot 2H_2O$: C, 40.5; H, 3.4; N, 15.8; Cl, 10.0. Found: C, 40.7; H, 3.4; N, 16.2; Cl, 10.0.

Bis-(pyridinaldazine)-iron(II) fluoroborate: blue-black crystals. *Anal.* Calcd. for $[Fe(C_{12}H_{10}N_4)_2](BF_4)_2$: C, 44.3; H, 3.1; B, 3.3; F, 23.4; Fe, 8.6. Found: C, 43.8; H, 3.1; B, 3.4; F, 23.1; Fe, 8.6.

Tris-(pyridinaldazine)-di-iron(II) perchlorate 2-hydrate: well-formed small maroon prisms. *Anal.* Calcd. for $[Fe_2(C_{12}H_{10}N_4)_3](ClO_4)_4 \cdot 2H_2O$: H, 2.9; N, 14.3; Cl, 12.1. Found: H, 3.3; N, 14.6; Cl, 12.0.[6]

Tris-(pyridinaldazine)-di-iron(II) fluoroborate 2-hydrate: red-black plate crystals. *Anal.* Calcd. for $[Fe_2(C_{12}H_{10}N_4)_3](BF_4)_4 \cdot 2H_2O$: C, 38.4; H, 3.1; B, 3.9; F, 27.0; Fe, 9.9. Found: C, 38.2; H, 3.1; B, 4.0; F, 26.1; Fe, 10.1.

Bis-(pyridinaldazine)-nickel(II) perchlorate 1-hydrate: shiny maroon crystals. *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_4)_2](ClO_4)_2 \cdot H_2O$: C, 41.4; H, 3.2; N, 16.1; Cl, 10.2. Found: C, 41.5; H, 3.6; N, 16.4; Cl, 10.2.

Bis-(pyridinaldazine)-nickel(II) fluoroborate 1-hydrate: shiny maroon crystals. *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_4)_2](BF_4)_2 \cdot H_2O$: C, 43.0; H, 3.3; Ni, 8.8; B, 3.2. Found: C, 43.0; H, 3.5; Ni, 10.9; B, 2.9.

Tris-(pyridinaldazine)-di-nickel(II) perchlorate 1-hydrate: pale yellow microcrystalline powder. *Anal.* Calcd. for $[Ni_2(C_{12}H_{10}N_4)_3](ClO_4)_4 \cdot H_2O$: C, 37.2; H, 2.7; N, 14.4; Cl, 12.2. Found: C, 37.5; H, 3.1; N, 14.5; Cl, 12.0.

Tris-(pyridinaldazine)-di-nickel(II) fluoroborate 1-hydrate: orange crystals. *Anal.* Calcd. for $[Ni_2(C_{12}H_{10}N_4)_3](BF_4)_4 \cdot H_2O$: C, 38.8; H, 2.9; B, 3.9; Ni, 10.6. Found: C, 38.8; H, 3.2; B, 3.8; Ni, 9.4.

Magnetic Measurements.—All magnetic measurements were made by the Gouy method, using an analyzed nickel chloride solution and water as standards. In Table I, column 2, are listed the measured molar susceptibilities, while the values in column 3 have been corrected for the diamagnetisms of ligand, anion and water of hydration. The molar diamagnetic corrections employed are: pyridinaldazine, -59×10^{-6}; perchlorate ion, -34×10^{-6};[7] iodide ion, -52×10^{-6};[7] water, -13×10^{-6}.[8] The average mean deviation is ± 0.04 Bohr magneton.

TABLE I

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF SOLID COMPLEXES

Compound[a]	$\chi_M \times 10^6$ (complex)	μ_{eff} per metal ion, B.M.
$[Fe(PAA)_2]I_2 \cdot H_2O$	+ 159	1.0
$[Fe(PAA)_2](ClO_4)_2 \cdot 2H_2O$	− 112	0.5
$[Fe(PAA)_2](BF_4)_2 \cdot H_2O$	− 66	0.6
$[Ni(PAA)_2]I_2 \cdot 2H_2O$	+3995	3.2
$[Ni(PAA)_2](ClO_4)_2 \cdot H_2O$	+4150	3.2
$[Ni(PAA)_2](BF_4)_2 \cdot H_2O$	+3675	3.1
$Fe_2(PAA)_3I_4 \cdot 2H_2O$	− 128	0.6
$Fe_2(PAA)_3(ClO_4)_4 \cdot 2H_2O$	+ 54	.7
$Fe_2(PAA)_3(BF_4)_4 \cdot 2H_2O$	− 271	.3
$Ni_2(PAA)_3I_4 \cdot 2H_2O$	+7070	3.0
$Ni_2(PAA)_3(ClO_4)_4 \cdot H_2O$	+7490	3.1
$Ni_2(PAA)_3(BF_4)_4 \cdot H_2O$	+7185	3.0

[a] PAA is 2-pyridinaldazine.

Conductivity Measurements.—Conductances were measured in 10^{-3} molar solutions at 25.0°, using an Industrial Instruments, Inc., Model RC-16B conductivity bridge, and a cell with $k = 1.400$ cm.$^{-1}$. The conductivity water for all measurements had a specific conductance of less than 4×10^{-7} ohm^{-1}.

(5) C. Harries and G. H. Lenart, *Ann.*, **410**, 101 (1915).

(6) Analysis difficult because of the explosive nature of the compound.

(7) P. W. Selwood, "Magneto Chemistry," 2nd Edition, Interscience Publishers, Inc., New York, N. Y., 1956, p. 78.

(8) Ref. 7, p. 86.

Analyses.—All analyses on non-metallic elements were performed by Galbraith Microanalytical Laboratories.

Results and Discussion

Two distinct types of pyridinaldazine complexes have been prepared in crystalline form as iodide, perchlorate, and fluoroborate salts with both iron(II) and nickel(II). The empirical formulas of these two types are: $M(PAA)_2X_2$ and $M_2(PAA)_3X_4$. The essential difference in the preparation of the two is not one of stoichiometric ratios of reactants, but rather of reaction conditions. In all cases, the three-to-two compounds are formed initially in solution, irrespective of the mole ratios of reactants. If crystallized fairly rapidly, this species may be isolated in pure form; however, if the solutions are heated on a steam-bath for a few minutes or allowed to stand, conversion to the two-to-one compounds takes place. In the case of iron(II) the conversion is accompanied by a distinct change in color, from red to blue. Consequently, spectrophotometric measurements in the visible provide a convenient method of studying this conversion. Measurements on a Cary Recording Spectrophotometer, Model 10, show an absorption peak for the red three-to-two compound at 4800 Å. and a peak for the blue two-to-one compound at 6500 Å. Furthermore, it is found that if a dilute solution of $Fe_2(PAA)_3I_4$ (10^{-4} molar) is allowed to stand for several days, a green solution is obtained which gives the absorption bands due to both compounds, whereas a concentrated solution of $Fe_2(PAA)_3I_4$ (0.1 molar) becomes deep blue upon standing, and has only the absorption band due to the two-to-one compound. Upon dilution of this blue solution, it slowly converts to the green solution, giving two bands. Thus an equilibrium is indicated. Only in concentrated solution is conversion to the blue two-to-one compound essentially complete. The solution phenomena are under investigation.

The $M(PAA)_2X_2$ compounds are of the expected type in which each ligand acts as a tridentate. Conductance data are in agreement with the formulation as a dipositive cation with two uni-negative anions. Table II lists the observed conductances of 10^{-3} molar solutions, together with specific cation conductances obtained by subtracting the known specific anion conductances in 10^{-3} molar solutions. The molar conductance of tris-(o-phenanthroline)-iron(II) chloride, $[Fe(o\text{-}phen)_3]Cl_2 \cdot 6H_2O$, measured in the course of the present work, is 201 ohms^{-1}, while the range given by Werner and Miolati[9] for a variety of amine complexes of this charge type is 234–268 ohms^{-1}. As would be expected on the basis of cation size, the PAA compounds are intermediate between the amines and the iron(II)-o-phenanthroline compound. The magnetic susceptibilities given in Table I indicate that the nickel compounds of this type contain paramagnetic nickel, while the iron compounds contain diamagnetic iron. Whether the small positive moments in the case of iron(II) (uniformly one Bohr magneton, or less) are associated with temperature independent effects or long lived excited states involving unpaired spins

(9) A. Werner and A. Miolati, *Z. physik. Chem.*, **14**, 508 (1894).

provides an interesting subject for further investigation.

Compound	$\Lambda_m(\text{ohm}^{-1})$	$\Lambda_{cation}(\text{ohm}^{-1})$
$Fe(PAA)_2I_2 \cdot H_2O$	210 ± 2	59
$Fe(PAA)_2(ClO_4)_2 \cdot 2H_2O$	198 ± 3	65
$Ni(PAA)_2I_2 \cdot 2H_2O$	224 ± 3	73
$Ni(PAA)_2(ClO_4)_2 \cdot H_2O$	192 ± 1	59

The structure of the $M_2(PAA)_3X_4$ compounds presents an intriguing problem. There can be little doubt that the empirical formulation is correct. Of the possible structures which the authors have considered, a dinuclear structure $[M_2(PAA)_3]X_4$ (structure V), in which each of three ligand molecules acts as a bidentate toward each of two metal ions, seems to be the most reasonable. This would result in a large tetrapositive cation with four univalent anions. Other possible structures are: one involving complex cation and anion $[M(PAA)_3][MX_4]$ (structure VI), and one which contains a complex salt and a free metal salt in the crystal in a one to one mole ratio, $[M(PAA)_3]X_2 \cdot MX_2$ (structure VII).

Conductance data for these compounds are given in Table III, along with data for several reference compounds of the MX_4 electrolyte type. It is observed that the values obtained are considerably lower than those for $[Pt(NH_3)_6]Cl_4$ and $K_4[Fe(CN)_6]$, but are intermediate between those of the two dinuclear compounds with large non-spherical complex ions, for which data are available. It is to be noted, however, that if structure VII with two MX_2 type electrolytes is assumed to be correct, the *average* molar conductances for these two electrolytes calculated on this basis are 213 ohm^{-1} (nickel compound, iodide salt) and 220 ohm^{-1} (iron compound, iodide salt), which is in satisfactory agreement with the values given for other MX_2 type complexes. Thus, conductivity data support both V and VII, but exclude structure VI. The magnetic data seem to exclude both VI and VII, however, since the iron is found to be essentially diamagnetic (Table I) whereas Fe^{++} and

Compound	$\Lambda_m(\text{ohm}^{-1})$	$\Lambda_{cation}(\text{ohm}^{-1})$
$Fe_2(PAA)_3I_4 \cdot 2H_2O$	441 ± 2	139
$Fe_2(PAA)_3(ClO_4)_4 \cdot 2H_2O$	403 ± 1	137
$Ni_2(PAA)_3I_4 \cdot 2H_2O$	427 ± 2	125
$Ni_2(PAA)_3(ClO_4)_4 \cdot H_2O$	371 ± 1	105
$[Pt(NH_3)_6]Cl_4$	523[9]	
$K_4[Fe(CN)_6]$	669[10]	
$[(dipy)_2Fe\underset{\diagdown OH}{\overset{\diagup OH}{\diagup\diagdown}}Fe(dipy)_2]Cl_4$	488[11]	
$K_4[(ox)_2Co\underset{\diagdown OH}{\overset{\diagup OH}{\diagup\diagdown}}Co(ox)_2]$	385[12]	

(10) G. Jones and F. C. Jelen, THIS JOURNAL, **58**, 2561 (1936).

(11) A. Gaines, Jr., L. P. Hammett and G. H. Walden, Jr., *ibid.*, **58**, 1668 (1936). (This value refers to a concentration of 5×10^{-4}.)

(12) E. G. Percival and W. Wardlaw, *J. Chem. Soc.*, 2628 (1929).

FeX_4^{--} would be paramagnetic with four unpaired electrons. The existence of perchlorate and fluoroborate salts of the $M_2(PAA)_3(X)_4$ type also militates against structure VI, since these anions have only very slight tendencies to coördinate with metal ions.

A reasonable structure for the $[M_2(PAA)_3]^{+4}$ ion is one in which each of the three ligand molecules acts as a bidentate group toward each of the two metal ions. If all four nitrogen atoms of each ligand are coördinated, the twelve apices of the octahedra around the two metal ions are filled. The resulting structure would be similar to the $W_2Cl_9^{-3}$ ion,[13] in which the two octahedra have one face in common, except that, in this case, the two adja-

(13) A. F. Wells, "Structural Inorganic Chemistry," Second Edition, Oxford University Press, London, 1950, p. 295.

cent faces are separated by the N–N bond distance. It can be shown, using models, that each of the three ligands will remain nearly planar, thus contributing to the stability of this structure. Earlier workers have prepared $(M_2trien_3)^{n+}$ compounds, where "trien" is the tetradentate triethylenetetramine,[14] but the nature of the preparations indicates that only one ligand acts as a bridge, with the other two ligands behaving as tetradentate chelating agents toward single metal ions. Such a structure does not seem reasonable for the compounds reported here, since pyridinaldazine cannot chelate in a tetradentate manner.

(14) F. Basolo, THIS JOURNAL, 70, 2634 (1948); H. B. Jonassen and B. E. Douglas, ibid., 71, 4094 (1949).

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Some Properties of Polymer Networks Formed from Oriented Chains of Natural Rubber

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Highly oriented natural rubber samples prepared by a modification of the racking process described by Feuchter were cross-linked by means of γ-radiation. Some of the physical properties of the networks prepared in this manner were studied and compared with networks formed from chains which were randomly arranged prior to the introduction of the cross links. In accord with the theoretical considerations of Flory it was found that the swelling behavior, isotropic length, and isotropic melting temperature of the networks depend not only on the fraction of units cross-linked but also very markedly on the arrangement of the chains prior to network formation. It also was observed that the crystalline oriented racked rubber was cross-linked twice as effectively by γ-radiation as was the amorphous rubber.

Introduction

A three-dimensional polymer network can be formed from an assemblage of individual polymer chains by the intermolecular linking of a sufficient number of chain elements. This intermolecular linking process is termed cross-linking and can be carried out by a variety of chemical methods and in favorable cases by the use of high energy radiation. The network that is formed differs in many of its properties from the original system of polymer chains. A polymer network is characterized by its insolubility, although it has the ability to imbibe many times its volume of liquid when immersed in a good solvent. A non-network collection of polymer chains, on the other hand, will completely dissolve under the same conditions. In the absence of crystallinity a polymer network is also characterized by its long range elasticity at temperatures above its glass temperature. Thus a network has the capacity to support a relatively large stress and to return to its original dimensions when the stress is removed.

In considering the physical and mechanical properties of polymeric networks, from both theoretical[1] and experimental[2] points of view, it always has been assumed that the cross-linking is a random process, i.e., units of different molecules are paired together in an uncoördinated and random manner, and furthermore that the polymer chains are in a

(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 464 ff.

(2) P. J. Flory, ref. 1, p. 577 ff.

randomly coiled configuration. The requirement that chain segments be randomly disposed prior to network formation is obviously a stringent limitation on the types of networks that can be formed. It is well known, for example, that many of the fibrous proteins occur naturally in a state of high orientation and cross-links if not already present can be introduced without disrupting the characteristic order of the system. Similarly, by a suitable mechanical and thermal treatment many of the more flexible chain-type molecules can be brought to states of high order and orientation and subsequently cross-linked. In a recent theoretical paper Flory[3] has considered the problem of how the properties of a network will depend on the relative arrangement of the chains prior to network formation. In this very general treatment the previous results for the more usual type network are deduced as a special case. The other extreme that can be conveniently considered is the case where the chains are perfectly axially oriented. It was found[3] that the properties to be expected in a network depend not only on the fraction of the units that are randomly cross-linked but also, in a significant manner, on the disposition of the chains prior to network formation. These theoretical deductions are important in efforts to explain the behavior and physical properties of both protein and non-protein macromolecular systems, and it is therefore of interest to assess, by experimental studies, their general validity.

(3) P. J. Flory, THIS JOURNAL, 78, 5222 (1956).