Electrical Semiconductivity of Stacked Layer Coordination Polymers of Rhodium(I)

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A study directed at the molecular design and preparation of unconventional coordination polymers with "tailor-made" chemical and/or physical properties yielded some novel tetragonal rhodium(I) polymers of the general type [Rh(aryl diisocyanide)$_2$$^+Cl^-$]$_n$.[1-5] A powder X-ray diffractometric trace analysis of these polymers revealed a stacked layer structure with an extensive network of columnar metal chains. A schematic representation of the three-dimensional structure of some coordination polymers of rhodium(I) with stereochemically rigid collinear linkages is shown in Figure 1. Further support for the presence of columnar metal chains in these polymers was obtained from their electronic spectra.[1,4] In view of the foregoing, it was considered of interest to examine the electrical conductivity of the polymers, a study reported herein.

Experimental Section

The [Rh(aryl diisocyanide)$_2$$^+Cl^-$]$_n$ polymers were prepared from [Rh(CO)$_2$Cl]$_2$ and the respective aryl diisocyanide ligands as previously reported.[1-5] The conductivity experiments described here were conducted on compressed-powder pellets (20 ton min^{-1} cm^{-2}) by the two-electrode method[6] (ac, 1 kHz) using a laboratory-designed holder apparatus and a 1680A digital automatic capacitance bridge assembly (General Radio Co., Concord, MA).

Results and Discussion

The room temperature (~25 °C) conductivities of these polymers (1.65×10^{-4} to 4.00×10^{-6} Ω^{-1} cm^{-1}) (see Table I) were found to be considerably higher than those reported for either Rh(CO$_2$)(acac) (10^{-11} Ω^{-1} cm^{-1}; E = 0.32–0.44 eV; Rh(I)–Rh(I), 3.26 Å)[7] or [Rh$_2$(CNPh)$_8$](BPh$_4$)$_2$ [7.2×10^{-11} Ω^{-1} cm^{-1}; Rh(I)–Rh(I), 3.19 Å].[8] Room temperature (25 °C) measurements conducted on a series of (alkyl and aryl isocyanide)rhodium(I) cations with TCNQ$^{\bullet-}$ as a radical anion, [Rh(CNR)$_4$]$^+$TCNQ$^{\bullet-}$[9] and [Rh(CNR)$_4$]$^+$(TCNQ)$_2$$^{\bullet-}$ showed these materials to have conductivities in the range 10^{-3} to $>10^{-10}$ Ω^{-1} cm^{-1}. In the temperature range 20–90 °C these complexes behave as typical semiconductors with activation energies of 0.065–0.55 eV.[9] A very recent report[10] on the oxidized Rh(III) systems, [Rh(RNC)$_4$I$_2$]$^+$-TCNQ$^{\bullet-}$ reveals room temperature (25 °C) conductivities in the range 10^{-3} to 10^{-6} Ω^{-1} cm^{-1} and for the complex salts [Rh(C$_6$H$_5$NC)$_4$I$_2$]$^+$(TCNQ)$_2$$^{\bullet-}$ and [Rh(4-MeC$_6$H$_4$NC)$_4$I$_2$]$^+$(TCNQ)$_2$$^{\bullet-}$, 8.3 Ω^{-1} cm^{-1} and 30 Ω^{-1} cm^{-1}, respectively. Activation energies for these latter systems, calculated in the temperature range 30–85 °C, are 0.043–0.39 eV. Additional higher conductivities were encountered for a series of cationic rhodium complexes[8] of the types [Rh(CNCH$_3$)$_4$]$^+$X$^-$ [X = Cl (3.3×10^{-2} Ω^{-1} cm^{-1}), BF$_4$ (2.2×10^{-2} Ω^{-1} cm^{-1})], [Rh(CNCH$_2$CH$_3$)$_4$]$^+$X$^-$ [X = Cl (6.7×10^{-4} Ω^{-1} cm^{-1}), ClO$_4$ (5.1×10^{-4} Ω^{-1} cm^{-1}), and PF$_6$ (3.9×10^{-5} Ω^{-1} cm^{-1})], and [Rh(CNCHCH$_2$)$_4$]$^+$X$^-$ [X = Cl (2.9×10^{-4} Ω^{-1} cm^{-1}), ClO$_4$ (5.6×10^{-3} Ω^{-1} cm^{-1}), and PF$_6$ (5.6×10^{-4} Ω^{-1} cm^{-1})] which contain Rh–Rh distances in the range 2.94–2.96 Å.

The conductivity of the compressed-powder pellets of the polymers with 1,4-diisocyanobenzene and 4,4′-diisocyanobiphenyl linkages was measured in the temperature range 25–150 °C. Thermal gravimetric analyses on these polymers[4] has shown decomposition to occur above 400 °C; therefore the temperature range chosen for conductivity measurements is an appropriate one. The results of the temperature-dependent conductivity study, expressed in the form of ln resistivity (ρ, Ω-cm) vs. $10^3/T$ [K^{-1}], are shown in Figure 2. Noteworthy are the nearly linear plots which allow the calculation of the respective band-gap energies according to the equation $\sigma = \sigma_0 \exp(-E/2kT)$, where σ ($=1/\rho$) stands for conductivity (Ω^{-1} cm^{-1}), and k and T stand for Boltzmann's constant (8.62×10^{-5} eV/deg) and absolute temperature (K), respectively. The calculated band-gap energies for the polymers with the 1,4-diisocyanobenzene [0.47 eV] and 4,4′-diisocyanobiphenyl [0.25 eV] linkages were obtained by accounting for all of the points along the respective plots (Figure 2). All conductivity measurements were conducted with ac techniques, and therefore the probability of interparticle contacts dominating the conductivity data is lessened.

The lower resistivity (ρ) and higher conductivity (σ) found for the 1,4-diisocyanobenzene rather than for the 4,4′-diisocyanobiphenyl polymer are consistent with the presence of a somewhat shorter (~0.1 Å) Rh(I)–Rh(I) bond distance in the former. The low resistivity and relatively high energy band gap found for the 1,4-diisocyanobenzene polymer may suggest that the conductivity in this system depends on additional factors apart from intermetallic interactions. In this regard, noteworthy are the orthogonal

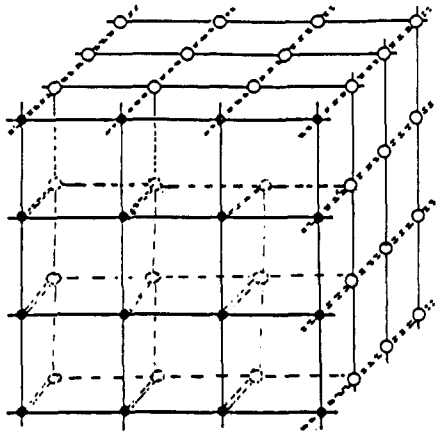

Figure 1. Schematic representation of the three-dimensional [Rh(diisocyanide)$_2$]$_2$ network in tetragonal coordination polymers of the type [Rh(diisocyanide)$_2$$^+Cl^-$]$_n$ with the collinear linkages (—) 1,4-diisocyanobenzene and 4,4′-diisocyanobiphenyl and columnar metal chains (---).

Table I
Electrical Conductivity Measurements of [Rh(aryl diisocyanide)$_2$$^+Cl^-$]$_n$ Polymers

aryl diisocyanide ligand	pellet thickness,[a] mm	Rh–Rh distance,[b] Å	measd conductivity, Ω^{-1}	specific conductivity, Ω^{-1} cm^{-1}
1,4-diisocyanobenzene	0.20	3.31	3.3×10^{-6}	1.65×10^{-4}
4,4′-diisocyanobiphenyl	0.50	3.40	6.1×10^{-7}	1.22×10^{-5}
1,3-diisocyanobenzene	0.20	*c*	8.0×10^{-8}	4.00×10^{-6}
4,4′-diisocyanodiphenylmethane	0.20	3.36	4.0×10^{-7}	2.00×10^{-5}
1,5-diisocyanonaphthalene	0.35	3.41	1.1×10^{-7}	3.14×10^{-6}

[a] Compressed powder pellets prepared under 20 ton cm^{-2} min^{-1}. Variation ±0.05 mm. [b] Bond distance data are those quoted in ref 4, a full manuscript submitted. [c] Not determined.

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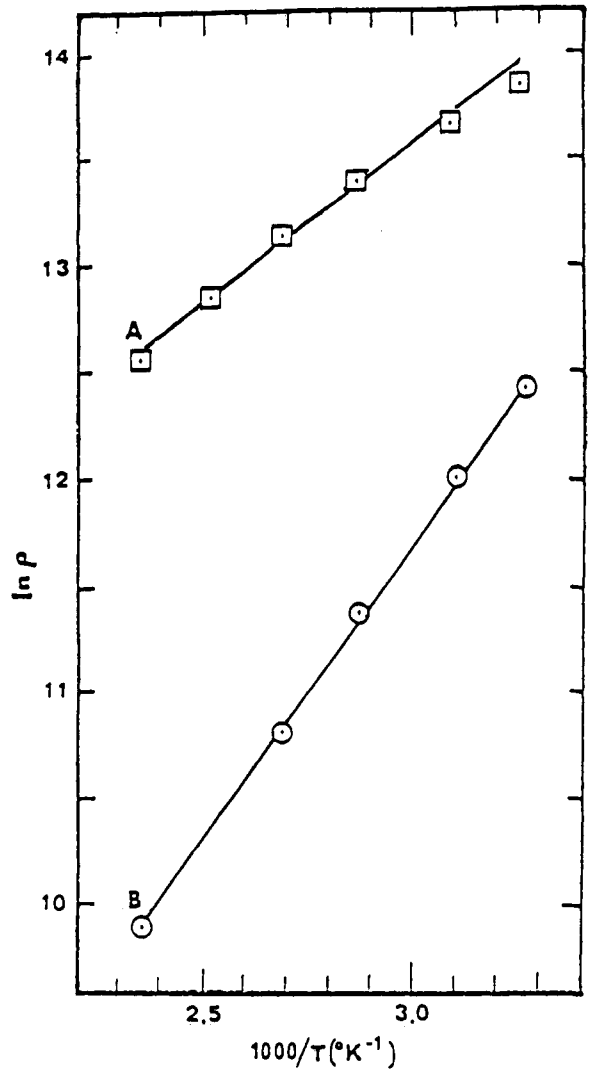

Figure 2. Temperature ($10^3/T$) dependence of the resistivity (ln ρ; Ω·cm) measured on compressed powder pellets of [Rh(4,4-diisocyanobenzene)$_2^+$Cl$^-$]$_n$ (A) and [Rh(1,4′-diisocyanobiphenyl)$_2^+$Cl$^-$]$_n$ (B).

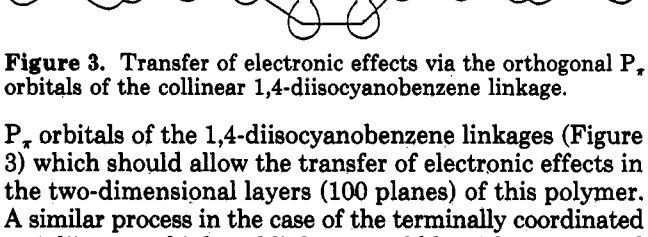

Figure 3. Transfer of electronic effects via the orthogonal P_π orbitals of the collinear 1,4-diisocyanobenzene linkage.

P_π orbitals of the 1,4-diisocyanobenzene linkages (Figure 3) which should allow the transfer of electronic effects in the two-dimensional layers (100 planes) of this polymer. A similar process in the case of the terminally coordinated 4,4′-diisocyanobiphenyl linkage would be either restricted or forbidden, depending on the dihedral angle of the phenylene rings of the biphenylene unit. The overall conductivity (σ) of these polymers should include intraplanar as well as interplanar contributions; the latter should be larger for the polymer with the 1,4-diisocyanobenzene linkages than for the 4,4′-diisocyanobiphenyl polymer. Anisotropic electrical properties may be determined by the study of single crystals. Unfortunately, the polymers under review have not yet been obtained in suitable crystallinic form to allow for such study.

The oxidation states of many of the cationic rhodium tetrakis(monoisocyanide) systems have been found to be greater than one (1.0–1.25).[8] This data may then suggest that these systems are one-dimensional metals in which the metallic behavior has been quenched by crystalline disorder and imperfections. On the other hand, the possibility of either a small band-gap intrinsic or extrinsic semiconductor systems, with the latter being dominated by Rh(II) "impurities", was also considered for these complexes.[8] Similar considerations may also apply to the coordination polymers reported herein.

Registry No. [Rh(1,4-diisocyanobenzene)$_2^+$Cl$^-$]$_2$, 74620-93-2; [Rh(4,4′-diisocyanobiphenyl)$_2^+$Cl$^-$]$_n$, 74620-95-4.

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Molecular Design of Multicomponent Polymer Systems. 8. New Acrylonitrile–Butadiene–Styrene-like Resins from Styrene–Acrylonitrile-Based Mechanical Blends

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One of the main applications of polymer blends is in the manufacture of impact-resistant materials, since phase separation is an essential feature for the rubber toughening of brittle plastics. In acrylonitrile–butadiene–styrene (ABS) resins, the rubbery phase usually consists of polybutadiene, nitrile rubber, or poly(styrene-*co*-butadiene) rubber (SBR). The largest part of the resins now manufactured is prepared by a graft copolymerization process of styrene and acrylonitrile in the presence of a preformed rubber.[1] Although mechanical blending remains certainly a very attractive and more versatile way toward these polyblends, it has important deficiencies that cause it to be less efficient than the copolymerization techniques. Among the necessary features of the rubber phase, good adhesion to the matrix, adequate cross-linking, and average particle diameter near the optimum value (ca. 0.5 μm) are the most important ones to achieve high impact performances.[2] These requirements are not met when melt blending styrene–acrylonitrile (SAN) with a commercial rubber. In order to alleviate that situation, we have investigated combinations of commercial thermoplastic elastomers in a SAN matrix, more precisely styrene–butadiene block copolymers (SBS) and appropriate polymeric

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