

Ordered Copper Aryldiisocyanide Polymers from Soluble Cu(I) Precursors

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Aryldiisocyanides are unique ligands that have been used successfully in the preparation of coordination organometallic polymers incorporating various transition metals: Rh [1, 2], Ir [2], Pd [3], Pt [3], W [4], Mo [4], Cr [4]. We have witnessed that both ordered [1, 2] and disordered [3, 4] macromolecular systems may result. In these materials, the degree of order cannot necessarily be determined in advance. Our research interests lie in the design and preparation of new materials with interesting chemical and physical properties. In this context, structure–property relationships have particular relevance, and therefore the investigation of the more ordered coordination aryldiisocyanide transition metal polymers may indeed be scientifically rewarding. Other authors have reported organometallic polymers of copper that have shown interesting catalytic [5] and electronic [6] properties, which encouraged our own efforts in this direction. We report here the preparation and characterization of $\{[\text{Cu}((\text{CN})_2\text{Ar})_2][\text{PF}_6]\}_n$ (Ar = C₆H₄, C₆H₄–C₆H₄) polymers.

Experimental

All solvents were dried and deoxygenated using accepted procedures.

Preparation of $\{[\text{Cu}((\text{CN})_2(\text{C}_6\text{H}_4-\text{C}_6\text{H}_4))_2][\text{PF}_6]\}_n$ Polymers

Via $[\text{Cu}(\text{NCCH}_3)_4][\text{PF}_6]$ precursors

The above precursor (200 mg, 0.55 mmol) was dissolved in acetonitrile (~25 cm³) and refluxed under Ar. The 4,4'-diisocyanobiphenyl ligand (272 mg, 1.3 mmol) in acetonitrile (~40 cm³) was slowly

dropped into the refluxing precursor solution. Within minutes a white fluffy precipitate appeared. The reaction was allowed to reflux overnight. The insoluble polymeric products were filtered and dried *in vacuo* (80 °C, 0.1 torr) to give quantitative yields of the above polymers. *Anal.* Found: C, 54.51; H, 2.72; N, 8.90; F, 18.32. Calc. for CuC₂₈H₁₆N₄PF₆: C, 54.50; H, 2.60; N, 9.00; F, 18.5%.

An analogous experimental procedure was used to prepare the $\{[\text{Cu}((\text{CN})_2(\text{C}_6\text{H}_4))_2][\text{PF}_6]\}_n$ polymers. *Anal.* Found: C, 41.35; H, 1.72; N, 12.04; F, 24.52. Calc. for CuC₁₆H₈N₄PF₆: C, 41.63; H, 2.00; N, 12.10; F, 25.0%.

Via $\text{Cu}(\text{OOCCH}_3)$ precursors

The above precursor (50 mg, 0.41 mmol) was placed in acetonitrile (~125 cm³) together with 70 mg (0.42 mmol) NaPF₆ and refluxed under argon. The 4,4'-diisocyanobiphenyl ligand (180 mg, 0.88 mmol) was added as in the above procedure. Again an almost immediate white precipitate appeared. The reaction was refluxed overnight to give quantitative yields of polymer 1.

Results and Discussion

Tetrakisarylimonoisocyanide copper(I) cationic complexes have recently been reported [7] starting with the same precursor complexes. However, a novel alternative preparative method employs Cu(OAc), prepared by the reduction of Cu(II) in Cu(OAc)₂ [8], which along with NaPF₆ did serve as a suitable starting material for the syntheses of $[\text{Cu}((\text{CN})_2\text{-Ar})_2\text{PF}_6]_n$ polymers. This reaction is not as rapid as in the case of the polymers prepared from $[\text{Cu}(\text{NCCH}_3)_4]\text{PF}_6$; however, under proper dilutions the last traces of acetate ligand can be substituted with aryldiisocyanides, as is evidenced by thermal gravimetric analyses (TGA). Other copper precursors, *i.e.* CuCl, although previously reported to give the monoisocyanide complexes $[\text{Cu}(\text{CNR})_4]^+$ (R = Ph and *p*-MeC₆H₄) [9], with these aryldiisocyanides yielded only mixtures of polymers in which the copper had not undergone total substitution with the aryldiisocyanides, and in which chloride ligands still remained. Attempts to prepare stabilized Cu(II) aryldiisocyanide polymers, regardless of the solution precursors involved, were unsuccessful. In accordance with previous observations [10], we observed an almost immediate reduction of the Cu(II) systems to Cu(I) aryldiisocyanide polymers.

Microanalyses indicate the formulation of these copper polymers to be $\{[\text{Cu}((\text{CN})_2(\text{C}_6\text{H}_4-\text{C}_6\text{H}_4))_2][\text{PF}_6]\}_n$ (1) and $\{[\text{Cu}((\text{CN})_2(\text{C}_6\text{H}_4))_2][\text{PF}_6]\}_n$ (2), both of which revealed sharp $\nu(\text{CN})$ peaks in diffuse

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reflectance infrared spectroscopy. For the former polymer, a band at $\sim 2160\text{ cm}^{-1}$ (vs) and a shoulder at $\sim 2122\text{ cm}^{-1}$ were observed, while the latter gave infrared absorbances at ~ 2172 (vs) and ~ 2130 (sh) cm^{-1} . The observed shoulders may be attributed to the non-coordinated peripheral isocyanide functionalities. These IR band positions are in the range of those reported from copper tetrakismonoisocyanide cationic complexes [7]. Interestingly, we observed a small ($\Delta \approx 6\text{ cm}^{-1}$) reversible shift to lower wave numbers in the $\nu(\text{CN})$ band of these polymers upon heating them from room temperature to 300°C . Similar but more significant reversible shifts ($\Delta \approx 12\text{ cm}^{-1}$) have been noted for the Rh(I) biphenyl tetragonal [1] and hexagonal [2] polymers upon exposing them to heat [11]. For the copper polymers, we have noted, in addition, reversible structural changes upon heating polymer 1 from 20°C to 180°C . Together with the IR data these results may indicate a redistribution of electron density upon the attainment or deviation of a linear or near linear $\text{Cu}-\text{C}\equiv\text{N}-\text{R}$ arrangement as a result of external heating. The copper and rhodium [1] aryldiisocyanide polymers are thermally stable in the temperature range cited above. TGA analyses on the copper aryldiisocyanide polymers under an argon atmosphere show a sharp decomposition occurs at $\sim 360^\circ\text{C}$.

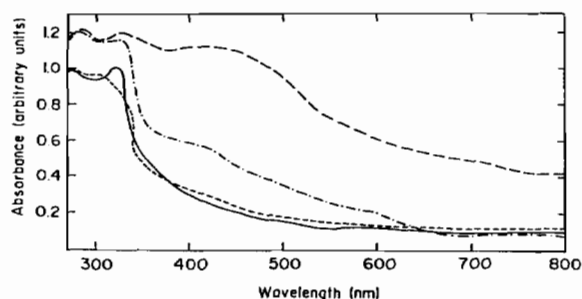


Fig. 1. Diffuse reflectance spectra of the $[\text{Cu}((\text{CN})_2\text{Ar})_2\text{PF}_6]_n$ polymers: (—) polymer 1; (---) polymer 1 under mechanical pressure of 10 ton cm^{-2} ; (— · —) polymer 2; (· · ·) polymer 2 under mechanical pressure of 10 ton cm^{-2} .

X-ray photoelectron spectroscopy shows a $\text{Cu } 2p_{3/2}$ band at 935.5 eV for polymer 1. No significant satellites were observed at higher binding energies and this is consistent with the Cu(I) oxidation state [12]. Diffuse reflectance spectra* of the 1 and 2 copper polymers are shown in Fig. 1. For the biphenyl polymer 1, a maximum is observed at $\sim 300\text{ nm}$ which shows a tailed shoulder absorption in the

*Compared to total reflectance and/or zero absorbance of a MgCO_3 standard, given in absorbance terms.

TABLE I. X-ray Powder Diffraction Angles [θ (deg)] and Assigned Indices (hkl) for Two Structural Modifications of Polymer 1

Polymer 1A ^a						Polymer 1B ^a							
θ^b	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{cal}}$	d (Å)	h	k	l	θ^b	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{cal}}$	d (Å)	h	k	l
4.100	0.00510	0.00516	10.76	1	0	0	4.225	0.0054	0.0055	10.45	0	0	1
5.825	0.01030	0.01032	7.59	1	1	0	5.300	0.0085	0.0084	8.34	1	1	0
7.525	0.01720	0.01734	5.88	1	1	1	9.588	0.0169	0.0168	4.62(vs)	2	0	0
8.325	0.02100	0.02064	5.32(vs) ^c	2	0	0	9.525	0.0274	0.0265	4.65	2	1	1
9.250	0.02580	0.02580	4.79	2	1	0	10.250	0.0324	0.0302,	4.33	1	1	2,
									0.0366		2	2	0
10.025	0.03030	0.03282	4.42	2	1	1	11.350	0.0387	0.0386	3.91	2	0	2
11.300	0.03840	0.03840	3.93	1	1	2	12.025	0.0434	0.0428	3.70(s)	2	1	2
11.975	0.04310	0.04128	3.72(s) ^c	2	2	0	12.825	0.0493	0.0491	3.47	0	0	3
13.125	0.05160	0.05160	3.39(s) ^c	3	1	0	13.350	0.0533	0.0533	3.33(s)	1	0	3
14.050	0.05890	0.05862	3.17	3	1	1	13.900	0.0577	0.0575	3.20(s)	1	1	3
15.800	0.07410	0.07452	2.83	3	0	2	15.425	0.0707	0.0714	2.89	4	1	0
16.775	0.08330	0.08256,	2.67	4	0	0,	19.300	0.1092	0.1092	2.33	5	1	0
		0.08382		2	0	3							
17.375	0.08920	0.08898	2.58	2	1	3	22.500	0.1465	0.1447,	2.01	1	1	5,
									0.1483		5	3	1
19.825	0.11500	0.01148	2.27	3	1	3	32.775	0.2931	0.2917	1.42	6	1	5
20.450	0.12210	0.02264	2.20	1	1	4	39.450	0.4037	0.4034	1.21	3	2	8
21.575	0.13520	0.13296,	2.09	2	0	4,							
		0.13602		5	0	1							

^aPolymer 1A: polymer 1 under inert, anhydrous conditions. Polymer 1B: polymer 1 in air. ^bBased on tetragonal symmetry, calculated from $\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + K^2) + \frac{\lambda^2}{4c^2}l^2$. Cell dimensions: polymer 1A, $a = 10.76\text{ Å}$, $c = 9.20\text{ Å}$; polymer 1B, $a = 11.90\text{ Å}$, $c = 10.45\text{ Å}$. ^cIntensities: (vs) = very strong, (s) = strong.

visible range. Polymer 2 does not show this shoulder absorption in the visible range. The spectral features of the above polymers were investigated after they were subjected to mechanical pressures of ~ 10 ton cm^{-2} and the resultant spectra are also shown in Fig. 1. We observe that the biphenyl polymer 1 changes from off-white to brown-gold in color, whereas there is no significant color change in polymer 2. Indeed in Fig. 1 we observe a greatly enhanced and slightly shifted visible absorption for polymer 1, while polymer 2 gives a very similar spectrum to that of the parent polymer without mechanical pressure. One possible explanation for the observed visible absorptions for polymer 1 may be attributed to $\pi-\pi^*$ transitions of the aryldiisocyanide ligands. The small red-shift in the broad shoulder band observed in the visible range for polymer 1 after application of mechanical pressure may be anticipated if an interaction between different ligand π -orbitals occurs [13]. Such an interaction may be expected if the Cu(I) centers could be compressed more closely to one another as a result of mechanical pressure.

Powder X-ray diffraction measurements have been performed on polymer 1 demonstrating the ordered nature of this system. Two structural modifications (A and B, respectively) have been identified and indexed (see Table I), the first attained under inert, anhydrous conditions, the second attained in air. One may note that both these polymers are indexed based on tetragonal symmetry, however, the cell dimensions in the case of polymer B are significantly greater. We have observed that occasional preparations of polymer 1A contain an additional polymer. This structural modification has been identified by powder X-ray diffraction as having cell dimensions $a = b = 17.06$ Å, $c = 3.92$ Å. These values are similar to those we have obtained for Rh(I) 4,4'-diisocyanobiphenyl polymers having square-planar geometry around the rhodium metal centers [1]. The presence or absence of this additional structural modification may be related to the relative concentration of copper precursor to aryldiisocyanide ligand, as in the case of the tetragonal and hexagonal modifications of the Rh(I) aryldiisocyanide polymers [2]. Based on the structural similarity to the Rh(I) aryldiisocyanide polymers, such mixtures probably contain different Cu(I) polymers, one having a square-planar geometry about the metal while the second has a tetrahedral geometry. Applying mechanical pressure (10 ton/ cm^3) to a solid mixture of these polymers gives new structural phases wherein the cell dimensions are compressed both in the x , y and z planes; however, these new phases have not yet been indexed completely. It is interesting to note

that similar cell compression phenomena have been noted as a result of heating this same solid mixture of polymers to 180 °C. Upon cooling, these polymers revert back to their original dimensions. Powder X-ray measurements on samples of polymer 2 have also been performed, revealing that these systems are structurally different from those of polymer 1 mentioned already, and perhaps this may explain the spectral differences noted for these two systems (Fig. 1).

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