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Simultaneous Polymerization and Crystallization: A New Method for the Preparation of Mixed-metal Coordination Polymers

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The usefulness of simultaneous polymerization and crystallization as a preparative tool for tansition metal polymers is established; syntheses of both stable and metastable mixed-metal (M=Ni,Co) polymers are described. The metastable polymers show solid-state reactivity as well as room-temperature photochromism.

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Simultaneous Polymerization and Crystallization: A New Method for the Preparation of Mixed-metal Coordination Polymers

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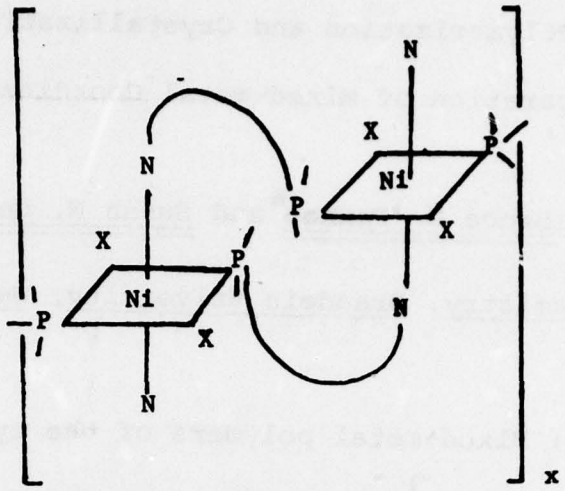
Summary: Mixed-metal polymers of the type $\{Ni_{0.5}Co_{0.5}Cl_2[P(CH_2CH_2CN)_3]_2\}_x$ have been prepared under various conditions; the low-temperature products have unusual properties, e.g. photochromism, and may be converted to the high temperature form in the solid state.

The preparation of solid, crystalline polymers has been reviewed recently.[1] However, the current technology has not often been applied in inorganic chemistry, e.g., to the production of transition-metal coordination polymers. We have previously demonstrated the high crystallographic and chemical specificity of a solid-state reaction leading to such polymers,[2] and report here the synthesis of mixed-metal polymers via simultaneous polymerization and crystallization.[3] The synthesis of polymeric NiX_2L_2 (where X = Cl, Br; L = $P(CH_2CH_2CN)_3$) has previously been reported by solid-state or solution techniques, and the complex has been shown to have the structure[2,4,5]



The mixed-metal polymer, $[Ni_{0.5}Co_{0.5}Cl_2L_2]_x$, may be prepared at ambient temperature by the reaction of equimolar amounts[6] of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ with an excess of L in an ethanol-acetone-triethylorthoformate (6:5:1) solution. A red precipitate [$NiCl_2L_2$ monomer, square planar] appears immediately in the purple solution. Solvent is then allowed to evaporate slowly; after loss of about 80% of the solvent, the $NiCl_2L_2$ monomer dissolves, and crystalline product forms rapidly, leaving a clear solution. In a typical preparation, three products are obtained: purple (~ 90%), green (~ 8%) and yellow (~2%) crystals. When the same reaction is carried out under reflux, a single product, deep blue in color, is obtained.

The low temperature preparation is rather unusual in that $3CoCl_2 \cdot 2L$, which is believed to have a trimeric cage structure of tetrahedrally coordinated Co(II),[5] does not form. $3CoCl_2 \cdot 2L$ is an exceptionally stable, intractable blue solid, which precipitates <u>immediately</u> upon addition of $CoCl_2 \cdot 6H_2O$ to an acetone

solution of L.

The mixed-metal polymer is characterized by the following properties:

(i) Upon rapid heating of the low temperature product the following color changes are observed:

$$\text{Purple}\,(\mu=3.94),\ \text{green or yellow} \xrightarrow{146^\circ\ C} \text{deep blue}\,(\mu=3.71) \xrightarrow{170^\circ\ C}$$

$$NiCl_2L_2\,(\text{monomer melt}) + 3CoCl_2{\cdot}2L\,(\text{solid})$$

Although the low-temperature materials transform rapidly and irreversibly at 146° to the deep blue form of the polymer, they are stable for 6-12 months at room temperature.

(ii) The purple crystals exhibit photochromic behavior. White-light irradiation causes the purple color to fade to a pale blue; if the light source is removed, the color returns to purple. The yellow and green polymers are <u>not</u> photochromic.

(iii) All four species are crystallographically identical and are isomorphous with the pure nickel polymer, $[NiX_2L_2]_x$.[2,4] However, differential scanning calorimetry indicates an endothermic change at ~ 146°, corresponding, e.g., to the purple → deep blue color change. The exact explanation for the various colors is unclear, but may involve "lattice strain", which shows some similar characteristics.[7]

In conclusion, we have found a useful method for the preparation of metastable coordination polymers with unusual properties. As pointed out by Wunderlich,[3b] one can expect perfect coupling of polymerization and crystallization near the ceiling temperature for that process, leading to unlimited size, perfection and molecular weight for a polymer. In the event that the simultaneous polymerization and crystallization occur far from the ceiling temperature, imperfect metastable crystals may result. Clearly, the former set of conditions apply to the high-temperature polymerization and the latter to the low-temperature process. These principles together with the experiments described herein suggest that simultaneous polymerization and crystallization techniques may have general utility for the production of both stable and metastable mixed-metal coordination polymers.

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