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

BRUCE M. FOXMAN* and SUSAN W. GERSTEN

Department of Chemistry, Brandeis University, Waltham, Mass. 02154, U.S.A.

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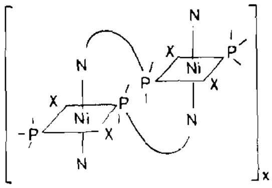
The preparation of solid, *crystalline* polymers has been reviewed recently [1]. However, the current technology has not often been applied in inorganic chemistry, *e.g.*, to the production of transition-metal coordination polymers. We have previously demonstrated the high crystallographic and chemical 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 a 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 *immediately* 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:

$$\text{Purple } (\mu = 3.94)\text{, green or yellow} \xrightarrow{146\ ^\circ\text{C}} \text{deep blue } (\mu = 3.71) \xrightarrow{170\ ^\circ\text{C}} NiCl_2L_2 \text{ (monomer melt)} + 3CoCl_2 \cdot 2L \text{ (solid)}$$

Although the low-temperature materials transform rapidly and irreversibly at 146 °C to a 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 *not* 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 °C, 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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*Author to whom correspondence should be addressed.

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