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An Introduction to the Solid State Polymerization of Transition-metal Complexes: A Comparative Study

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An Introduction to the Solid State Polymerization of Transition-metal Complexes

A Comparative Study

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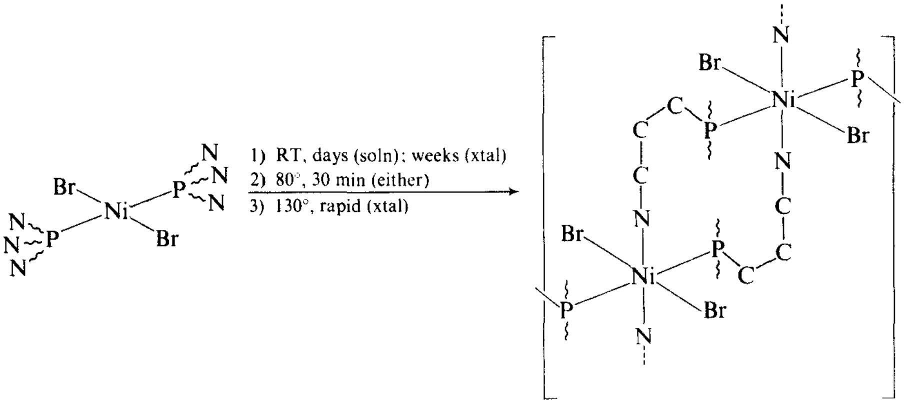
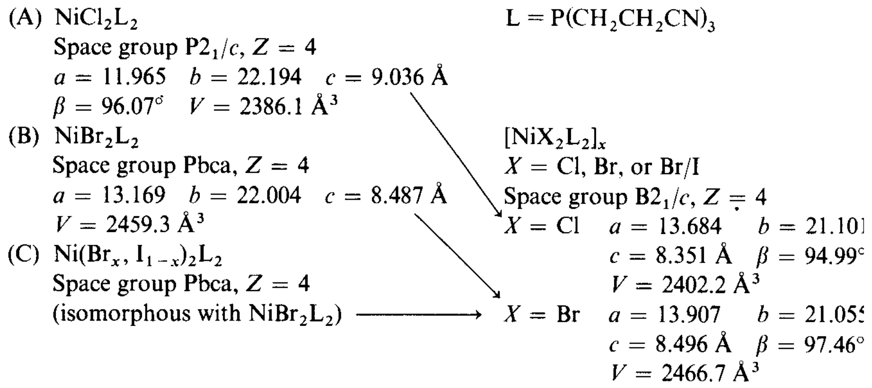
Preliminary studies in this laboratory[1] of topochemical and topotactic polyreactions of $NiBr_2[P(CH_2CH_2CN)_3]_2$ have shown that the reactions are in many cases characterized by a) product specificity, b) stereospecificity, c) "crystallographic specificity" and d) highly anisotropic "front motion" through individual single crystals. The polymerization reaction under investigation here is



Scheme I

Here we extend the study to the analogous chloride and iodide-doped bromide complexes. These are viewed in an intercomparative sense, and conclusions are drawn regarding the general features of topochemical topotactic and anisotropic reactions in solids.

An overview of this system is presented in the scheme below:



(A) $NiCl_2L_2$
Space group $P2_1/c$, $Z = 4$
$a = 11.965$ $b = 22.194$ $c = 9.036$ Å
$\beta = 96.07°$ $V = 2386.1$ Å^3

(B) $NiBr_2L_2$
Space group Pbca, $Z = 4$
$a = 13.169$ $b = 22.004$ $c = 8.487$ Å
$V = 2459.3$ Å^3

(C) $Ni(Br_x, I_{1-x})_2L_2$
Space group Pbca, $Z = 4$
(isomorphous with $NiBr_2L_2$)

$L = P(CH_2CH_2CN)_3$

$[NiX_2L_2]_x$
X = Cl, Br, or Br/I
Space group $B2_1/c$, $Z = 4$
X = Cl $a = 13.684$ $b = 21.10$
$c = 8.351$ Å $\beta = 94.99$
$V = 2402.2$ Å^3
X = Br $a = 13.907$ $b = 21.05$
$c = 8.496$ Å $\beta = 97.46°$
$V = 2466.7$ Å^3

Scheme II

Thus, this is a rather remarkable system, in that three unique monomer phases, each of which behaves differently as the solid-state polymerization proceeds (*vide infra*), all lead to an identical, isomorphous polymeric product phase. Our studies of this system have allowed us to explore the interplay of nucleation phenomena, and the geometrical aspects of reactivity, lattice shear and solid-state growth mechanisms. Formally, we were led to consider the above phenomena by studying the two major sequential aspects of this solid-state reaction, *viz.*, (i) chemical propagation and (ii) daughter (product) phase growth.

1 CHEMICAL PROPAGATION

In all three monomer systems, the chemical propagation of the reaction may be deduced by considering the crystal structures of monomer and polymer. Scheme II reveals that all polymeric phases are isomorphous, while the monomer phases are isomorphous except for the case where X = Cl. Despite these differences, there is an overwhelming similarity: the polymerization occurs along [101] and/or [10$\bar{1}$] directions in the monomer crystals. This is evident from the following observation: in both monomer and polymer phases, the nickel complexes occupy the centers of symmetry (0, 0, 0), (1/2, 0, 1/2), (0, 1/2, 1/2) and (1/2, 1/2, 0). Further, examination of the polymer crystal structure shows that Ni complexes at (0, 0, 0) and (1/2, 0, 1/2) form part of a linear polymer chain, while complexes at (1, 1/2, 1/2) and

(1/2, 1/2, 0) form part of a second chain. Indeed, this is the expected topochemical product based on the least-motion principle.[3] We conclude, therefore, that polymerization occurs only between Ni complexes in specific *ac* planes. This conclusion, based on crystal structures of reactant and solution-grown product, is only valid if the polymer phase produced *via* solid-state reaction is identical to that grown from solution. Fortunately, these reactions are *topotactic*, which has allowed us to observe reactant and product phases simultaneously on an x-ray photograph. This feature confirms the identical nature of the single-crystal-grown and solution-grown phases.

2 ANISTROPY OF THE REACTION

For all three reactions outlined in Scheme II, highly anisotropic front motion—in the form of a red-to-blue change in reacting crystals—is observed. However, the nature of this anisotropic motion varies greatly depending upon which monomer system is under consideration. For reaction (A) the (initially) wine-red monomer crystals begin to turn blue (polymerization) at a large number of sites; as the reaction proceeds, the blue areas grow with elongation in (roughly) the [101] and $[10\bar{1}]$ directions. Thus, this reaction is characterized by multiple nucleation, followed by poorly-defined anisotropic propagation from each site.

Reaction (B) differs markedly from (A): a blue area appears on a (100) face of a monomer crystal and propagates along [001] rapidly. This leads to the reactant (100) face being "coated" with polymer phase. The remainder of the reaction occurs with well-defined front motion along the [100] direction of the reactant crystal. Inspection of crystals as they are just beginning to react indicates that nucleation begins at a single area on a (100) face.

Finally, in reaction (C), nucleation begins at one "end" of the crystal, and well-defined front motion occurs approximately along [201]. While there are no (102) faces on the reactant crystal,[2] surface nucleation appears to begin at a point on the crystal which is consistent with the development of [201]—front motion.

3 DAUGHTER PHASE (POLYMER) GROWTH AND TOPOTAXY

The topotactic relationships between monomer and polymer crystals, as obtained from x-ray diffraction studies (Weissenberg photographs) of reacting single crystals, are given in Table I. It is notable that reaction (B) generally shows only a single product orientation, while (A) and (C) show

TABLE I

Topotactic Relationships Between Monomer and Polymer Crystals

Compound	Relationship
$NiCl_2L_2$	$b_p \parallel b_m$; a_p + 4.7° from a_m; also a_p − 5.8° from a_m (two orientations of a_p corresponding to two twin individuals)
$NiBr_2L_2$	$b_p \parallel b_m$; $c_p \parallel c_m$; a_p 7.5° away from a_m. (Relationship holds for a "single-face" nucleation only—see text)
$NiBr_{1.86}I_{0.14}L_2$	$b_p \parallel b_m$; $a_p \parallel [201]_m$ (Again, as in polymeric $NiCl_2L_2$, two twin individuals are present)

at least two product orientations, consistent with the principle of conservative twinning[4] and the observations and principles established for polymerization of diacetylene monomer crystals.[3] We suggest that the apparently anomalous behavior of (B) results from an unusual type of nucleation on a single crystal face, followed by an epitaxial growth of product in (100) planes.

4 PREPARATION OF COORDINATION POLYMERS BY SOLID STATE REACTIONS[5]

Upon rapid heating, the following color changes are observed: (M, P = solid monomer and polymer, respectively, and U = polymeric product of unknown constitution.)

$NiCl_2L_2$: M(red) $\xrightarrow{134^\circ}$ P(blue) $\xrightarrow{183^\circ}$ M(red) $\xrightarrow{185^\circ}$ red oil
$NiBr_2L_2$: M(red) $\xrightarrow{132^\circ}$ P(blue) $\xrightarrow{151^\circ}$ U(green) $\xrightarrow{164^\circ}$ red-green oil
NiI_2L_2: M(red) $\xrightarrow{140^\circ}$ red oil
$NiBr_{1.86}I_{0.14}L_2$: M(red) $\xrightarrow{128^\circ}$ P(green) $\xrightarrow{155^\circ}$ red oil

One of the most striking features of the above scheme is the high solid-state reactivity of these systems. Further, this reactivity varies markedly with the halogen bound to the nickel. Thus,

i) where X = Cl, the polymerization is *reversible* in the solid state. The initial red monomeric material obtained from solution is a kinetic product, and polymerizes slowly at room temperature or rapidly at elevated temperatures. The high- and low-temperature monomer phases are crystallographically identical;

ii) where X = Br, the polymerization is *not* reversible in the solid state. Heating at temperatures of ~150°C produces a limited amount of randomly-oriented green polymer, which has defied characterization.

iii) where $X = \mathrm{I}$, polymerization does not occur. However, the NiI_2L_2 monomer is isomorphous with $NiBr_2L_2$ monomer. A solid solution of the two materials has quite different polymerization properties from the pure $NiBr_2L_2$ monomer (*vide supra*).

It is important to note in this section that experiments described in sections 1, 2 and 3 of this report pertain only to solid-state polymerization carried out in the temperature range −20 to +30°C. At temperatures above 50°C, random nucleation occurs throughout the crystal volume, and polycrystalline pseudomorphs are produced. There is no evidence of topotaxy for reactions carried out at temperatures above 50°C.

5 PREPARATION OF COORDINATION POLYMERS BY SIMULTANEOUS POLYMERIZATION AND CRYSTALLIZATION

All of the coordination polymers described in this report are highly insoluble in all media. Excellent single crystals of the polymers may be grown by simultaneous polymerization and crystallization[6] from acetic acid/acetone solutions of the respective monomer when the solutions are kept at ~50°C for 24 hours. In general, it is these crystals which have been used to study the crystal structures of the polymers. Recent work in these laboratories has shown that simultaneous polymerization and crystallization is an excellent technique for incorporating other transition metal ions, e.g., Co^{2+}, into the polymer chain. If the experiments are carried out under kinetically-controlled conditions, metastable, photochromic polymers with high stability (~1 year at room temperature) may be obtained.[7]

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