Isolation and characterization of a unique heterocyclic ring system from nickel-ion catalysed polymerization of phenylisocyanide

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Nickel-ion catalysed polymerization of phenylisocyanide (PhNC) produces the expected major product, poly(*N*-phenyliminomethylene), and a minor product of low molecular mass with a structure that gives insight into the mechanism of polymerization.

The nickel(ii) catalysed polymerization of isocyanide derivatives has been formulated as producing helical structures by a process described as a 'merry-go-round mechanism'.[1] Intermediates that seem to confirm this proposed mechanism[2] have been isolated and the structures of these characterized nickel(ii) complexes have been established.[3] Recently, Deming and Novak[4] have challenged the assumption that Ni[II] is the active catalytic centre; their data implicating Ni[I] as the centre around which the helical polymers are constructed.

In the hopes of taking advantage of the interesting helical polymers that can be produced when isocyanide derivatives are catalytically polymerized, we embarked upon a study of the polymerization process as applied to phenylisocyanide (PhNC). As part of these studies we reported that the 'as-prepared' poly(*N*-phenyliminomethylene) **I**[5] is indeed substantially helical when first formed mechanistically but that dissolution of **I** in a non-polar solvent leads to an unravelling of the helical conformation. Our conclusion from this study, along with speculation in the literature,[6] is that the 'merry-go-round mechanism' is applicable initially but subsequent processing of the resultant helical polymers is liable to lead to non-helical structures if the side-chain group is not sterically demanding.[7]

As part of our initial investigation we reported[5] that polymer **I** is always accompanied by a low molecular mass component which is produced in very low yield when the polymerization is carried out in methanol as described.† We have now characterized the low molecular mass component from the polymerization of PhNC, structure **II** in Scheme 1, and this leads to some interesting conclusions concerning the polymerization mechanism. Structure **II** is unique[8] in the chemical literature‡ and allows us to speculate on the 'merry-go-round mechanism'[1] and its application when Ni[I] is the active catalytic centre.[4]

Preparation of the 'as-prepared' polymer **I** and GPC analysis of this polymer has been described elsewhere.[5] The bulk of the soluble product consisted of a polymer with $M_n \approx 2000$ and broad polydispersity but GPC always showed a low molecular mass band whose intensity was dependent upon the method of polymerization; those preparations done under a blanket of N$_2$ had a much more pronounced low molecular mass peak than those done under ambient air. Isolation of this low molecular mass fraction from the GPC column led to a colourless, crystalline solid with mp 263.5–264 °C. From preparations that yielded 2 g of the 'as-prepared' polymer **I** we were able to isolate about 20 mg of **II** when a blanket of N$_2$ was employed during the reaction.

The isolated crystalline solid **II** was structurally characterized by high-resolution mass spectrometry and ^{1}H and ^{13}C NMR and IR spectra. The high-resolution mass spectrum, using NH$_4$[+] in the LSIMS mode, yielded an (M+H)[+] molecular ion with $m/z = 550.22353$ which most closely fits the molecular formula C$_{35}$H$_{27}$N$_5$O$_2$.§ The ^{1}H NMR spectrum displays 27 protons of which 23 resonate as a complex multiplet centred at

δ 7.25 while the remainder resonate as doublets at δ 5.89 (1H, $J = 2$ Hz), 6.03 (2H, $J = 7$ Hz) and 6.52 (1H, $J = 2$ Hz). The ^{13}C NMR spectrum exhibits 35 signals with peaks at δ 166.0, 151.5 and 150.5 assigned to imine carbons, those at δ 146.2, 144.2, 140.8, 138.1 and 135.0 are assigned to *ipso* carbons on the phenyl rings, 25 peaks between δ 130.2 and 119.2 are associated with *o*-, *m*- and *p*-carbons on the phenyl rings, and two at δ 74.6 and 67.0 which are assigned to saturated bridgehead carbons.¶ The [1]H–[13]C HETCOR spectrum connects the δ 5.89 proton to the δ 74.6 carbon and the δ 6.52 proton to the δ 67.0 carbon.‖ The [1]H–[13]C COLOC (long-range HETCOR) correlates the δ 5.89 proton with both the δ 151.5 and 166.0 carbons and the δ 6.52 proton with both the δ 150.5 and 151.5 carbons. Finally, the IR spectrum shows a strong absorption at 1668 cm^{-1} assigned to an imine stretching mode. The spectral information is compatible with structure **II**.

The mechanism that is implied by the isolation of **II** accommodates both the 'merry-go-round'[1] concept and the idea that Ni[I] is the active catalytic centre,[4] as indicated in Scheme 1. Initiation of the process begins with the formation of **A**[3] and if an amine nucleophile is present, and a sterically hindered
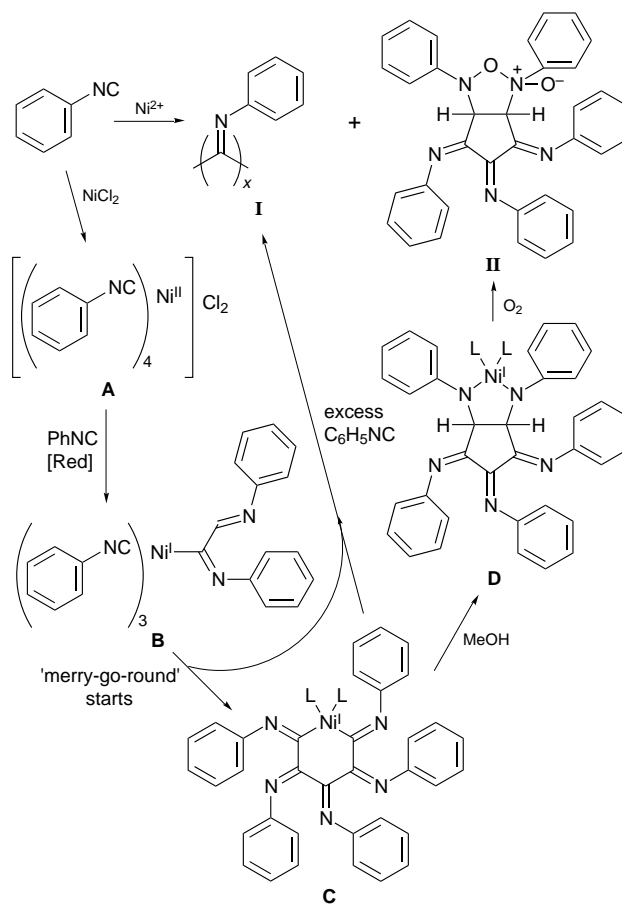
Scheme 1

isocyanide derivative is being polymerized, then a nickel(**ii**)–carbene intermediate can be isolated.[9] However, in the absence of a good nucleophile (such as an amine), attack by the reducing isocyanide (in excess) should lead to the intermediate **B** which contains a nickel(**i**) carboiminoyl diradical moiety rather than a nickel(**ii**) carbene moiety.[9] The intermediate **B** can initiate the 'merry-go-round' for which the activation barrier is very low and the polymerization proceeds until either O_2 terminates the reaction or isocyanide is depleted. Under anaerobic conditions the chain-growth process is slowed[4] because of an increased activation barrier that leads through **C** to products (again, the presence or absence of an excess of isocyanide determines the ultimate course of reaction). The enhanced stability of **C** may be due to the fact that the pentamer corresponds to the first turn of a 4_1 helix and this puts the fifth monomer in a geometry to readily coordinate to the metal. From **C**, when either depletion of isocyanide or anaerobic conditions dictate the course, the solvent (MeOH) acts as a reducing agent which leads to an intermediate such as **D**, which should be isolable. Once O_2 is introduced into the system, intermediate **D** is quickly oxidized to **II** and the Ni^{II} regenerated.**

Footnotes

† *Polymer preparation*: PhNC was added to a stirred solution of anhydrous $NiCl_2$ in MeOH, either under a blanket of N_2 or in contact with air, and the mixture was stirred for one week. A solid precipitate began to form after a short time and polymerization was virtually complete within one or two days but the odour of PhNC was still present so that stirring was always continued for one week. The solid precipitate was removed by filtration, washed thoroughly with MeOH, dried, and analysed by GPC.[5]

‡ An unstable intermediate (2,3,5-triphenyltetrahydro-1,2,5-oxadiazole-*N*-oxide) having a similar structure to **II** has been isolated[8] but little spectral information is available for it. Compound **II** shows some decomposition after several months but is much more stable than intermediates reported in the literature.[8]

§ The observed *m/z* value of 550.22353 for $(M + H)^+$ deviates from the calculated value for $C_{35}H_{28}N_5O_2^+$ of 550.22370 by < 0.73 ppm. Anal. Calc. for $C_{35}H_{27}N_5O_2$ C, 76.48; H, 4.95; N, 12.74. Found, C, 76.08; H, 5.14; N, 12.37%.

¶ A DEPT spectrum confirmed the assignment of the quaternary carbons.

‖ Based on the size of the coupling constant, the ring fusion seems to be in the *cis* conformation. MM2 calculations show that the *cis* isomer is of lower energy than the *trans* isomer, supporting this conclusion.

** We have noted that the amount of **II** produced is approximately the same as the molar amount of $NiCl_2$ used to initiate the catalysis, but how intermediate **C** evolves into intermediate **D** is still unclear. We have been unable to isolate either **C** or **D** and we have been unable to characterize the oxidation product derived from the presumed reducing agent, methanol.

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