Polymerisation of acrylonitrile with di(organoimido)chromium(VI) complexes

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[(Bu^{t}N)$_2$Cr(CH$_2$Ph)$_2$] 1 and [(NCMe$_2$CH$_2$CH$_2$CMe$_2$N)Cr-(CH$_2$Ph)$_2$] 2 are robust single-component catalysts for the polymerisation of acrylonitrile, which afford high-molecular-weight PAN and also allow acrylonitrile–methyl methacrylate copolymerisation; owing to its strained seven-membered chelate ring, 2 exhibits exceptionally small imido bond angles.

The polymerisation of α-olefins by titanocene- and zirconocene-based catalysts is of great technological relevance.[1] Nevertheless, there is increasing interest in the development of novel non-metallocene catalysts for olefin polymerisation, since these may allow, *inter alia*, an even greater control over polymer properties. Several new catalyst families have been described in this context,[2] one of them being di(organoimido)chromium(VI) complexes of the type (RN)$_2$CrX$_2$ (X = Cl, Me, CH$_2$Ph),[3] which have proved to be excellently suited to the polymerisation of ethylene in the presence of a cocatalyst.[4] Owing to their comparatively low Lewis acidity, catalysts based on group 6 metals may be more tolerant towards polar, functionalised olefins than group 4 metal systems. For example, complexes of the type (RN)$_2$CrCl$_2$ have been shown to tolerate ester groups in the cyclopropanation of olefins.[5] We report here on the polymerisation of acrylonitrile by di(organoimido)chromium(VI) complexes.

We have utilised [(Bu^{t}N)$_2$Cr(CH$_2$Ph)$_2$][3a] 1 and the novel *ansa*-di(organoimido) complex [(NCMe$_2$CH$_2$CH$_2$CMe$_2$N)-Cr(CH$_2$Ph)$_2$] 2‡ as catalysts. 2 bears an isolobal relationship to group 4 *ansa*-metallocene derivatives.[6] Its structure has been determined by single-crystal X-ray diffraction (Fig. 1)§ and resembles that of 1.[3b] Both compounds contain an η^1- and an η^2-benzyl ligand. In solution, however, only one set of ^{1}H NMR resonances is observed for the two benzyl ligands even at low temperatures owing to rapid averaging. The most striking differences between 1 and 2 are due to the strained seven-membered chelate ring present in 2, which causes exceptionally small imido bond angles (Table 1). A similar structural effect was recently observed in the chemistry of molybdenum.[6a] A variable-temperature ^{1}H NMR study (500.1 MHz, [^{2}H$_8$]toluene solvent) reveals that the chelate ring is moderately flexible in solution. At room temperature, a single, averaged signal at δ 1.82 is observed for the four protons of the CH$_2$CH$_2$ unit, which is compatible with an averaged C$_{2v}$-symmetric structure. The singlet shows coalescence at *ca.* −10 °C. At −70 °C two well separated signals (2 × 2 lines) are observed at δ 1.25 and 2.35, which is in agreement with the AA′BB′ spin system expected for a rigid C$_2$-symmetric ligand framework. ΔG$^{\#}$ is *ca.* 48 kJ mol^{-1} for the ring inversion.

Table 1 Comparison of bond lengths (pm) and angles (°) in 1 and 2

	1	**2**
Cr–N	162.5(2)/163.2(2)	163.1(3)/163.3(3)
N–Cr–N	116.09(8)	104.19(16)
Cr–N–C	166.07(13)/160.60(13)	146.8(3)/147.3(3)

Complexes 1 and 2 are active catalysts for the polymerisation of the polar, functionalised olefin acrylonitrile (AN). No cocatalyst is needed.¶ In all cases studied the polymerisation started immediately and continued for an extended period of time (Fig. 2). Initially, the polyacrylonitrile (PAN) yield increased linearly, and during the course of the reaction it approached an upper limit. After a while the clear solution became cloudy and a white precipitate was observed. At the same time the viscosity started to increase. The molecular weight reached remarkably high values, and the polydispersity (M_w/M_n) decreased slightly with the conversion (Fig. 2). The PAN produced by 1 and 2 had approximately the same tacticity (Table 2).[7] Copolymerisation experiments were performed with acrylonitrile and methyl methacrylate (MMA). The low glass
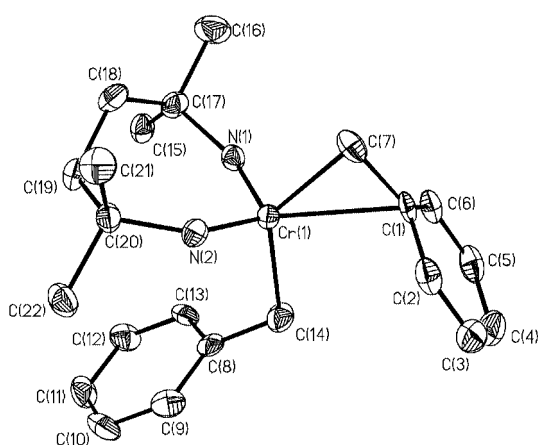

Fig. 1 Molecular structure of **2** in the crystal. Selected bond lengths (pm) and angles (°): Cr(1)–C(1) 242.0(4), Cr(1)–C(7) 207.0(4), Cr(1)–C(14) 208.5(4), N(1)–C(17) 146.6(5), N(2)–C(20) 145.9(5); C(1)–Cr(1)–C(7) 37.03(14), Cr(1)–C(7)–C(1) 84.6(2), C(7)–Cr(1)–C(14) 130.89(16), Cr(1)–C(14)–C(8) 113.9(3).
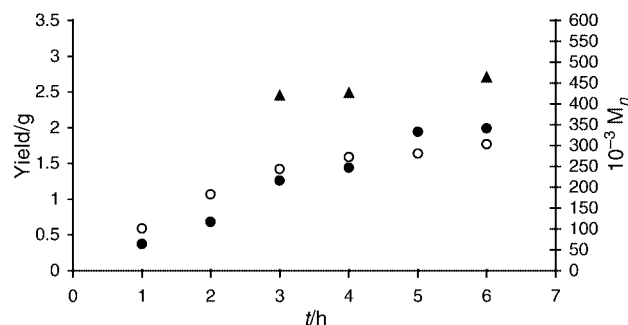

Fig. 2 Polymerisation of acrylonitrile with **1** and **2** {PAN yields [(●) **1**, (○) **2**] and molecular weights [(▲) **2**]}: Molecular weights and polydispersity for **2** after 3/4/6 h: M_n = 420 000/427 000/464 000; M_w = 1 200 000/1 200 000/1 300 000; M_w/M_n = 2.9/2.8/2.8.

Table 2 The triad microtacticity of polyacrylonitrile as obtained from 75.5 MHz ^{13}C NMR spectra in [^{2}H]$_6$DMSO

Specified group	Triad tacticity (%)		
	mm	mr	rr
Cyano	31[a]	45[a]	24[a]
	25[b]	48[b]	27[b]
Methine	27[a]	53[a]	20[a]
	27[b]	52[b]	21[b]

[a] **1**. [b] **2**.

Table 3 Results of acrylonitrile–methyl methacrylate copolymerisation runs using **1** and **2**

Run	AN/mmol	MMA/mmol	Yield/g	$T_g{}^a$/°C
1[b]	400	100	2.02	84.64
2[b]	100	400	4.57	92.04
3[c]	200	100	0.94	78.63
4[c]	75	150	0.71	87.49

[a] T_g (PMMA) = 128 °C and T_g (PAN) = 144 °C with **1** and **2**. [b] **1**. [c] **2**.

transition temperature T_g in comparison with T_g of the respective homopolymer PAN and PMMA indicates that the products obtained must be copolymers (Table 3).

The metal-catalysed polymerisation and copolymerisation of acrylonitrile is unprecedented. We are currently investigating the polymerisation mechanism. We note that with rigid ligand architectures of appropriate symmetry the formation of stereoregular functionalised polyolefins may be feasible, if the polymerisation mechanism is essentially metal-centered.

Notes and references

‡ Complex **2** was synthesised in analogy to the three-step route developed for **1**, starting from the silylated diamine (Me$_3$Si)HNCMe$_2$CH$_2$CH$_2$-CMe$_2$NH(SiMe$_3$) and CrO$_2$Cl$_2$. *Selected spectroscopic data*: δ_H(500.1 MHz, CDCl$_3$, 298 K) 7.00 (m, 10 H, Ph) 2.53 (s, 4 H, CH_2Ph) 1.83 [br s, 4H, (CH$_2$)$_2$], 0.99 (s, 12H, Me). δ_C(125.8 MHz, CDCl$_3$, 298 K) 141.0 (C$_{ipso}$ Ph) 130.8 (C$_{ortho}$ Ph) 129.0 (C$_{meta}$ Ph) 124.9 (C$_{para}$ Ph) 74.2 (C Me$_2$) 43.7 (CH$_2$Ph) 40.6 [(CH$_2$)$_2$] 27.4 (Me). MS (CI) *m/z* 375 (100%) [M]$^+$.
§ *Crystal data* for **2**: C$_{22}$H$_{30}$CrN$_2$, *M* = 374.5, monoclinic, space group *P*2$_1$/*n*, *a* = 8.471(4), *b* = 16.716(10), *c* = 14.781(6) Å, β = 100.21(3)°, *V* = 2059.9(18) Å^3, *Z* = 4, μ(Mo-Kα) = 0.561 mm^{-1}, *F*(000) = 800, orange plate (0.6 × 0.4 × 0.1 mm), 2θ_{max} = 50.0°, 3886 reflections measured, 3627 unique (R_{int} = 0.0558) which were used in all calculations; *R*(*F*) = 0.0570 for 2346 reflections with *I* > 2σ(*I*), *wR*(*F*^{2}) = 0.1222 for all data. A single crystal was mounted in inert oil and transferred to the cold gas stream of a Siemens P2$_1$ four-circle diffractometer. The structure was solved using direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on *F*^{2} (programmes used: Siemens SHELXTL PLUS and SHELXL 97).

CCDC 182/1659. See http://www.rsc.org/suppdata/cc/b0/b002310h/ for crystallographic files in .cif format.

¶ *Experimental procedures*: polymerisations of acrylonitrile were carried out under argon in a 100 ml flask equipped with a magnetic stirrer and a cooling jacket. Typically, polymerisations were run with 0.012 mmol of **1** or **2** and 300 mmol of acrylonitrile in toluene solution (40 ml) at 20 °C. The reactions were carried out in the dark to exclude radical formation, since usually polyacrylonitrile is prepared by radical polymerisation. The reactions were quenched with methanol. The white fine powder which precipitated was filtered off and dried *in vacuo* at 60 °C for 12 h. Copolymerisation experiments with acrylonitrile and methyl methacrylate were made under essentially identical conditions, utilising 0.02 mmol of **1** or **2** in toluene solution.

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