

- [5] W. Grünert, N. W. Hayes, R. W. Joyner, E. S. Shapiro, M. Rafiq, H. Siddiqui, G. N. Baeva, *J. Phys. Chem.* **1994**, *98*, 10832–10846.
- [6] a) G. Spoto, S. Bordiga, D. Scarano, A. Zecchina, *Catal. Lett.* **1992**, *13*, 39–44; b) G. Spoto, A. Zecchina, S. Bordiga, G. Ricchiardi, G. L. Martra, G. Leofanti, G. Petrini, *Appl. Catal. B* **1994**, *3*, 151–172.
- [7] The XANES spectrum of the sample before CO dosage (not reported) shows a prominent pre-edge peak due to the $1s \rightarrow 4p$ electronic transition, with an intensity of 0.88 in normalized adsorption and an inflection point at 8982.7 eV (-0.15 Ry in the scale of Figure 3). Note that the zero energy point (0.00 Ry) has been located by the program CONTINUUM^[22] at 8984.8 eV. Upon formation of $\text{Cu}^I(\text{CO})_3$ complexes (top curve in Figure 3) the peak loses intensity (0.42 in normalized adsorption) and shifts towards lower energies (8981.2 eV i.e. -0.26 Ry). For comparison, note that the first inflection point in Cu foil, Cu_2O and CuO model compounds are observed at 8979.0, 8980.9 and 8983.9 eV respectively (i.e. -0.43 , -0.29 and -0.07 Ry). A real energy calibration was achieved by measuring the absorption of a metal foil located after the sample, for more detail see: G. Turnes Palomino, P. Fiscaro, E. Giamello, S. Bordiga, C. Lamberti, A. Zecchina, *J. Phys. Chem. B* **2000**, *104*, 4064–4073.
- [8] C. Lamberti, S. Bordiga, F. Geobaldo, M. Salvalaggio, G. Spoto, A. Zecchina, G. Vlaic, M. Bellatreccia, *J. Phys. Chem. B* **1997**, *101*, 344–360.
- [9] L. Rodriguez-Santiago, M. Sierka, V. Branchadell, M. Sodupe, J. Sauer, *J. Am. Chem. Soc.* **1998**, *120*, 1545–1551; D. Nachtigallová, P. Nachtigall, M. Sierka, J. Sauer, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2019–2026.
- [10] a) A. J. Lupinetti, S. Fau, G. Frenking, S. H. Strauss, *J. Phys. Chem. A* **1997**, *101*, 9551–9559; b) R. Ramprasad, W. F. Schneider, K. C. Hass, J. B. Adams, *J. Phys. Chem. B* **1997**, *101*, 1940–1949; c) M. Sodupe, V. Branchadell, M. Rosi, C. W. Bauschlicher, Jr., *J. Phys. Chem. A* **1997**, *101*, 7854–7859.
- [11] A. Zecchina, S. Bordiga, G. T. Palomino, D. Scarano, C. Lamberti, M. Salvalaggio, *J. Phys. Chem. B* **1999**, *103*, 3833–3844.
- [12] a) S. Bordiga, C. Lamberti, G. T. Palomino, F. Geobaldo, D. Arduino, A. Zecchina, *Microporous Mesoporous Mater.* **1999**, *30*, 129–135; b) G. Schulz, S. Ernst in *Handbook of Heterogeneous Catalysis*, Vol. 1 (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), VCH, Weinheim, **1997**, pp. 374–387.
- [13] J. J. Rack, J. D. Webb, S. H. Strauss, *Inorg. Chem.* **1996**, *35*, 277.
- [14] For a brief overview on the $\tilde{\nu}(\text{CO})$ of different $\text{Cu}^I(\text{CO})$ complexes, see D. Scarano, S. Bordiga, C. Lamberti, G. Spoto, G. Ricchiardi, A. Zecchina, C. Otero Areán, *Surf. Sci.* **1998**, *411*, 272–285, or S. H. Strauss, *J. Chem. Soc. Dalton Trans.* **2000**, 1–6.
- [15] The intrazeolitic $\text{Cu}^I(\text{CO})$ complex is characterized by a single band at $\tilde{\nu}(\text{CO}) = 2157 \text{ cm}^{-1}$. This frequency compares well with that of $[\text{Cu}^I(\text{CO})]^+$ in superacidic media^[3] and of $[\text{Cu}(\text{CO})]^+[\text{Cl}]^-$ ($\tilde{\nu}(\text{CO}) = 2127 \text{ cm}^{-1}$, M. Håkanson, S. Janger, *Inorg. Chem.* **1990**, *29*, 5241–5243) and $[\text{Cu}(\text{CO})]^+[\text{HB}(3,5\text{-(CF}_3)_2\text{Pz}_3)]^-$, Pz = pyrazolyl, ($\tilde{\nu}(\text{CO}) = 2137 \text{ cm}^{-1}$, H. V. R. Dias, H.-L. Lu, *Inorg. Chem.* **1995**, *34*, 5380–5382).
- [16] The observation of an IR-active doublet ($\tilde{\nu}(\text{CO}) = 2151$ and 2178 cm^{-1}) indicates that the intrazeolitic $\text{Cu}^I(\text{CO})_2$ adducts have local C_{2v} symmetry, while the homogeneous counterpart in $[\text{Cu}^I(\text{CO})_2]^+ \text{AsF}_6^-$ ^[13] is linear ($D_{\infty h}$). Recently, Strauss et al. reported the stabilization of the dicarbonylcopper(I) ion by larger anions: $[\text{Cu}^I(\text{CO})_2]^+[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ and $[\text{Cu}^I(\text{CO})_2]^+[(1\text{-Bn-CB}_{11}\text{F}_{11})]^-$ have bent C_{2v} $\text{Cu}^I(\text{CO})_2$ moieties like those observed in ZSM-5: O. G. Polyakov, S. M. Ivanova, C. M. Gaudinski, S. M. Miller, O. P. Anderson, S. H. Strauss, *Organometallics* **1999**, *18*, 3769–3771; S. M. Ivanova, S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, S. H. Strauss, *Inorg. Chem.* **1999**, *38*, 3756–3757. The formation at room temperature of dicarbonyls indicates that there is a strong similarity between the chemistry towards CO of Cu^I in superacidic media (where they are in contact with extremely weak basic anions like AsF_6^-) and in Cu^I -ZSM-5 (where the role of counteranion is assumed by a zeolite anion). This result is in agreement with the fact that the conjugate acid H-ZSM-5 is very strong (like trifluoromethanesulfonic acid: C. Pazé, S. Bordiga, C. Lamberti, M. Salvalaggio, A. Zecchina, G. Bellussi, *J. Phys. Chem. B* **1997**, *101*, 4740–4751).
- [17] The IR spectrum of the $\text{Cu}^I(\text{CO})_3$ complex shown in Figure 1a (solid line) was obtained after the subtraction of the band at 2138 cm^{-1} , which is presumably due to liquidlike CO physisorbed in the zeolite channels (S. Bordiga, D. Scarano, G. Spoto, A. Zecchina, C. Lamberti, C. Otero Areán, *Vib. Spectrosc.* **1993**, *5*, 69–74). This band was previously wrongly attributed by us to a third component of the tricarbonyl adduct.^[6b, 8]
- [18] a) D. C. Koningsberger, R. Prins, *X-Ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York, **1988**; b) H. Bertagnolli, T. S. Ertel, *Angew. Chem.* **1994**, *106*, 16; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 45–66.
- [19] P. S. Braterman in *Metal Carbonyl Spectra in Organometallic Chemistry* (Eds.: P. M. Maitlis, F. G. A. Stone, R. West), Academic Press, London, **1975**.
- [20] The parallel IR investigation was fundamental, since it allowed the p_{CO} needed to obtain complete formation of the $\text{Cu}^I(\text{CO})_3$ complexes at 80 K to be determined and the XANES data for clusters having C_{3v} symmetry to be simulated.
- [21] a) A. Filippini, A. Di Cicco, C. R. Natoli, *Phys. Rev. B* **1995**, *52*, 15122–15134; b) A. Filippini, A. Di Cicco, *Phys. Rev. B* **1995**, *52*, 15135–15149.
- [22] a) C. R. Natoli, M. Benfatto, *J. Physique (Colloque C8)* **1986**, *47*, 11–23; b) T. A. Tyson, K. O. Hodgson, C. R. Natoli, M. Benfatto, *Phys. Rev. B* **1992**, *46*, 5997–6019.
- [23] J. G. Norman Jr., *Mol. Phys.* **1976**, *31*, 1191–1198.

Nickel-Catalyzed Generation of Schiff Base Aluminum Enolate Initiators for Controlled Methacrylate Polymerization**

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Many methods have been described that bring about the controlled polymerization of acrylate monomers^[1] including, for example, classical anionic techniques,^[2] screened anionic polymerization (SAP),^[3] group-transfer polymerization (GTP),^[4] catalytic chain transfer (CCT),^[5] reversible addition–fragmentation chain transfer (RAFT),^[6] atom transfer radical polymerization (ATRP),^[7] TEMPO-mediated free radical polymerization (TEMPO = 2,2,6,6-tetramethyl-1-piperidinoxyl),^[8] and coordination polymerization systems based on electrophilic metal centers such as samarium,^[9] zirconium,^[10] and aluminum.^[11] There continues to be great

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academic and commercial interest in the development of systems for the controlled polymerization of acrylate monomers, especially robust, commercially viable systems that will enhance the syndiotactic content to give higher softening temperatures in commodity polymers such as poly(methylmethacrylate) (PMMA).^[12]

For polymerizations mediated by electrophilic metals such as Sm, Zr, and Al, there is good evidence that metal enolates are the propagating species and, in the case of samarium, Yasuda and co-workers have isolated and structurally characterized a key enolate intermediate.^[9] Enolate species are also believed to play a central role in aluminum-mediated polymerizations, although direct evidence has been less forthcoming, and in general they appear to form less readily than their rare earth relatives.

In ground-breaking work on aluminum, Inoue and co-workers demonstrated that the porphyrin complex [Al(tpp)Me] (tpp = 5,10,15,20-tetraphenylporphyrinato), upon irradiation with visible light, forms a living (or "immortal") polymerization system.^[11] The visible radiation has been shown to assist the formation of the active aluminum enolate initiator. However, the potential drawbacks of this system are twofold: 1) the use of a ligand that carries an intense chromophore can impart serious discolorations to the poly(acrylate) products; and 2) the requirement for a light source to facilitate the efficient formation of an enolate species in the case of [Al(tpp)Me]^[13] restricts potential commercial applications.

Here we describe a remarkably active and robust aluminum initiator system based upon the tetradentate 'N₂O₂' Schiff base ligand frame ('N₂O₂' = *N,N'*-ethylenebis(salicylideneimine)) [Eq. (1)] and a novel nickel-catalyzed approach to

generating the active aluminum enolate centers. The Schiff base ligand system was chosen for three principal reasons: 1) in general, Schiff base compounds are easily prepared by simple condensation procedures that are readily amenable to ligand backbone modification; 2) the resultant aluminum Schiff base complexes are significantly less colored than their porphyrinato analogues; and 3) the aluminum centers are anticipated to be more electrophilic in the Schiff base derivatives due to replacement of two nitrogen atoms by two oxygen atoms in the ligand core, which possibly offers polymerization centers of enhanced activity. Complexes of this type have been the focus of interest in other areas of catalysis^[14] and alkoxyaluminum derivatives have recently been exploited^[15, 16] in the stereoselective ring-opening polymerization (ROP) of lactide monomers.

The nickel-catalyzed approach to active enolate centers builds on the observation by Jeffery et al.^[17] that [Ni(acac)₂] can be used to catalyze the reaction of trimethylaluminum with α,β -unsaturated carbonyl species to give aluminum enolates in high yield. In this study, we focus on the Schiff base methylaluminum complex [Al(*t*Bu₄salen)Me] (**1**) (*t*Bu₄salen = 3,3',5,5'-tetra-*tert*-butyl-salen), a derivative with particularly good solubility in a range of solvents.^[18] The results of polymerization studies on methylmethacrylate are summarized in Table 1.

On its own, compound **1** is not a good initiator for MMA polymerization (entry 1), affording only 8 % conversion after 20 h, to give PMMA of high molecular weight and broad molecular weight distribution. Bis(2,6-di-*tert*-butyl-4-methylphenoxide)aluminummethyl (MAD) is widely used as a Lewis acid activator for MMA polymerizations,^[11b] and addition of three equivalents of MAD to **1** is found to increase the rate of reaction and conversion (entry 2), but it also dramatically increases the molecular weight of the resultant PMMA. Entries 3 and 4 show that neither MAD nor [Ni(acac)₂] on their own are capable of initiating the polymerization of MMA, although in combination these reagents give a highly active, albeit not well-controlled, polymerization system (entry 5). When [Ni(acac)₂] is combined with **1** in the absence of MAD, a poor initiating system is again obtained (entry 6).

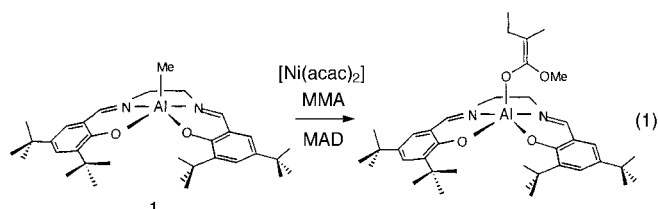


Table 1. Results of MMA polymerizations.^[a]

Entry	1	MAD	[Ni(acac) ₂]	Time	% Yield ^[b]	<i>M_n</i> ^[c]	<i>M_w</i> / <i>M_n</i>	% <i>r_r</i> ^[d]	% <i>mm</i> ^[d]
1	1	0	0	20 h	8	184 000	2.54	69	3
2	1	3	0	20 h	87	2 × 10 ⁶	2.86	72	3
3	0	3	0	20 h	0	—	—	—	—
4	0	0	1	20 h	0	—	—	—	—
5	0	3	1	< 2 min	95	118 300	1.63	72	2
6	1	0	1	20 h	7	229 400	1.85	71	2
7	1	3	1	< 2 min	92	24 700	1.17	69	3
8 ^[e]	1	3	1	< 2 mins	90	26 000	1.18	68	2
9 ^[f]	1	3	1	1 h	77	23 000	1.14	72	1
10 ^[g]	1	3	1	1 h	22	15 600	1.17	71	1
11 ^[g]	1	3	1	2 h	46	25 700	1.17	72	2
12 ^[g]	1	3	1	3 h	54	27 300	1.25	71	2
13 ^[g]	1	3	1	3.5 h	60	30 400	1.26	71	1
14 ^[g]	1	3	1	4 h	75	35 700	1.22	72	1

[a] Unless stated otherwise, conditions employed are: 1.00 g MMA (200 equiv, target *M_n* 20 000) in 2 mL CH₂Cl₂. [b] Yield after workup, polymer precipitated from acidified MeOH, washed 3 times with MeOH, then dried for 12 h (60 °C, 5 Torr). [c] Determined by GPC using monodisperse poly(styrene) standards. [d] Determined by ¹H NMR spectroscopy. [e] Reaction carried out in toluene. [f] Reaction carried out in THF. [g] 2.00 g MMA (400 equiv, *M_n* targeted at 100 % conversion = 40 000) in 4 mL THF.

It is only when $[\text{Ni}(\text{acac})_2]$ is combined with **1** and MAD in a three-component system that a highly active and well controlled polymerization results, affording PMMA of pre-determined molecular weight and narrow molecular weight distribution (entries 7 and 8). These observations suggest that the MAD reagent plays a dual role, one of activating the MMA monomer, the other of generating the active nickel catalyst responsible for enolate formation (see below).

Upon addition of the MMA solution (CH_2Cl_2 or toluene) to a 1:1:3 ratio of **1**, $[\text{Ni}(\text{acac})_2]$, and MAD, there is an immediate color change from pale green to bright orange, associated with the formation of a new nickel species along with the active aluminum initiator. There is a large exotherm and the reaction is complete inside two minutes, after which the solution color rapidly changes from orange to dark brown; the system is then no longer active. The syndiotactic (*rr*) content of the resultant PMMA is ca. 70% in all cases, and can be raised to 84% (< 1% *mm*) by carrying out the polymerization at -20°C . Pentad analyses on the carbonyl carbon signals in the ^{13}C NMR spectrum (triad test: $-4[rr][mm]/[mr]^2 = 0.7$ and $2[rr]/[mr] = 4.7$) suggests that the PMMA is formed by a chain-end control mechanism (see Supporting Information for more details).

Experiments in which the concentration of $[\text{Ni}(\text{acac})_2]$ is varied from 0.05 to 2 equivalents relative to $[\text{Al}(\text{tBu}_4\text{salen})\text{Me}]$ show no effect on the molecular weight or molecular weight distribution of the resultant PMMA, which confirms that the nickel component plays a catalytic role and that the polymerization is not nickel-centered. There is a linear relationship between M_n and $[\text{mon}]/[\text{I}]$ (Figure 1 a), narrow molecular weight distribution PMMA being formed in each case, and varying the amount of MAD activator does not affect the molecular weight of the polymer formed, only the rate of reaction. This provides good evidence that the polymerization is centered at the Schiff base ligated aluminum, rather than the aluminum center of the activator.^[19]

The polymerization is significantly slower in THF (entry 9), attaining only 77% conversion after 1 h, presumably due to competition for the active site between monomer and THF. On reaching 100% conversion in THF, darkening of the solution is not observed, the system remains active and displays living characteristics. A plot of M_n versus percentage conversion (Figure 1 b, Table 1, entries 10–14) reveals a linear relationship and narrow distribution product. A prepolymer solution generated in this manner can be used to bring about the formation of block copolymers. For example, addition of 200 equivalents of MMA to the initiator system followed by 141 equivalents of *n*-butylmethacrylate affords a PMMA-*b*-PBMA copolymer. Figure 2 shows the GPC traces for the PMMA prepolymer and the PMMA/PBMA block copolymer. A small amount of “dead” prepolymer can be seen as a low molecular weight tail to the GPC trace of the di-block product indicating that a small proportion of the prepolymer chains have died before re-initiation with BMA.

In order to probe further the role of $[\text{Ni}(\text{acac})_2]$, its reaction with the efficient alkylating agent $[\text{Me}_2\text{Al}(\text{OEt})]$ was studied. Upon mixing the aluminum and nickel species in CH_2Cl_2 , an immediate reaction was observed to give a brown solution reminiscent of the decomposition reaction following polymer-

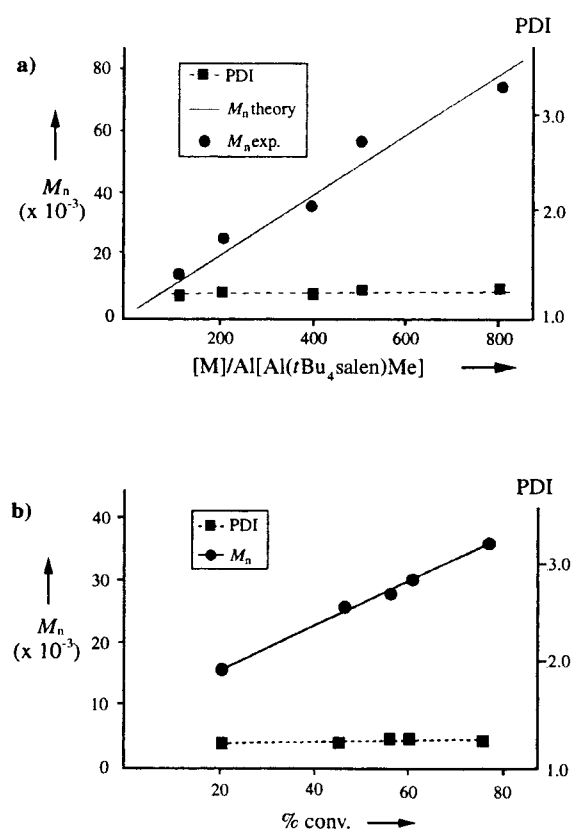


Figure 1. a) Plot of M_n versus $[\text{mon}]/[\text{tBu}_4\text{SalenAlMe}]$ (CH_2Cl_2 solution, $[\text{Ni}(\text{acac})_2]:[\text{Al}(\text{tBu}_4\text{salen})\text{Me}]:\text{MAD}:\text{MMA} = 1:1:3:x$, where $x = 100, 200, 400, 500, 800$); b) plot of M_n versus % conversion (THF solution, $[\text{Ni}(\text{acac})_2]:[\text{Al}(\text{tBu}_4\text{salen})\text{Me}]:\text{MAD} = 1:1:3$).

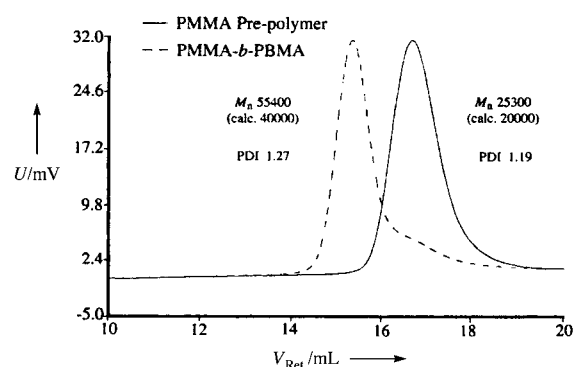
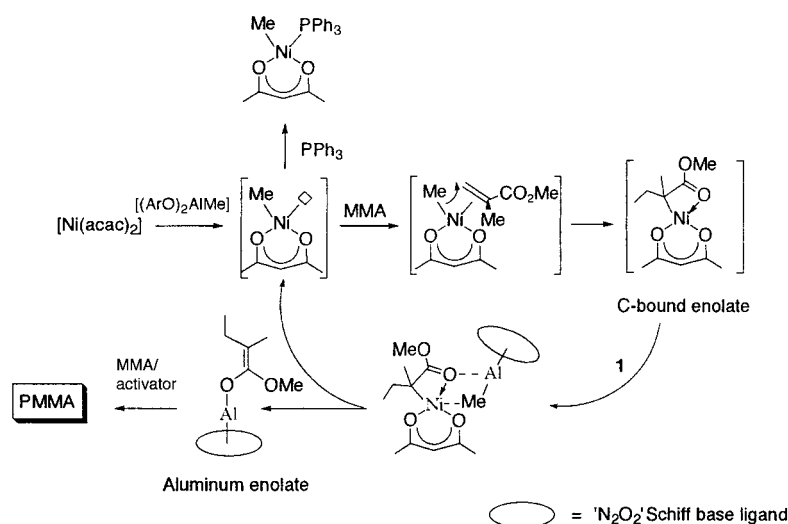


Figure 2. GPC traces for the PMMA prepolymer and the PMMA-PBMA di-block copolymer.

ization. When the same reaction was carried out in the presence of PPh_3 , the known complex $[\text{Ni}(\text{acac})(\text{Me})(\text{PPh}_3)]^{[20]}$ was formed, indicating that a key function of the activator is to abstract an acac ligand and to alkylate the nickel center which, in the presence of PPh_3 , is stabilized as the phosphane adduct (acac = acetylacetonato). The reaction with MAD, though more difficult to follow by NMR, is also believed to result in alkylation of the nickel center. In the absence of phosphane it is presumed that MMA will bind to the nickel center (Scheme 1), where it is then available to insert into the Ni–C(methyl) bond to give a carbon-bound enolate species. This species is apparently stable only in the presence of excess MMA. It is, therefore, probable that an



Scheme 1. Postulated mechanism for the role of nickel in the catalyzed formation of aluminum enolates.

additional equivalent of MMA binds to the nickel center, possibly in place of the carbonyl group (Scheme 1). To account for the catalytic dependence of the reaction on $[\text{Ni}(\text{acac})_2]$ and the fact that the polymerization is centered at the $\text{Al}(\text{tBu}_4\text{salen})$ component, transfer of the enolate from nickel to aluminum with concomitant transfer of the methyl group from aluminum to nickel is proposed (Scheme 1). This generates the active aluminum enolate species for polymerization and reforms the “[$\text{Ni}(\text{acac})\text{Me}$]” catalyst. In a separate study we have successfully synthesized the aluminum enolate species, $[\text{Al}(\text{tBu}_4\text{salen})\{\text{OC}(\text{ORBu})=\text{CMe}_2\}]$, and shown that this is an efficient initiator for MMA polymerization. These results will be reported in due course.

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- [1] T. P. Davis, D. M. Haddleton, S. N. Richards, *Macromol. Chem. Phys.* **1994**, C34, 243.
- [2] a) K. Hatada, K. Kitayama, K. Ute, *Prog. Polym. Sci.* **1988**, 13, 189; b) S. Nakahama, A. Hirao, *Prog. Polym. Sci.* **1990**, 15, 299; c) W. Szwarc, *Adv. Polym. Sci.* **1983**, 49, 1.
- [3] D. G. H. Ballard, R. J. Bowles, D. M. Haddleton, S. N. Richards, R. Sellens, D. L. Twose, *Macromolecules* **1992**, 25, 5907.
- [4] O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. Rajan Babu, *J. Am. Chem. Soc.* **1983**, 105, 5706.
- [5] a) A. F. Burczyk, K. F. O'Driscoll, G. L. Rempel, *J. Polym. Sci. Polym. Chem. Ed.* **1984**, 22, 3255; b) N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev, I. M. Belgovskii, *J. Polym. Sci. Polym. Chem. Ed.* **1981**, 19, 879; c) A. H. Janowicz, *US-A Patent* 4694054, **1987**. [*Chem Abstr.* **1987**, 106, 157018.]
- [6] J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, 31, 5559.
- [7] a) C. Granel, P. Teyssié, P. DuBois, P. Jérôme, *Macromolecules* **1996**, 29, 8576; b) D. M. Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek, A. Shooter, *Chem. Commun.* **1997**, 683; c) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, 28, 1721; d) V. Percec, B. Barboiu, *Macromolecules* **1995**, 28, 7970; e) K. Matyjaszewski, *Curr. Opin. Solid State Mater. Sci.* **1996**, 1, 769, and references therein.
- [8] a) D. Mardare, K. Matyjaszewski, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1993**, 34, 566; b) R. P. N. Veregin, M. K. Georges, P. M. Kazmaier, G. K. Hamer, *Proc. Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.* **1993**, 68, 8.

- [9] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* **1992**, 114, 4908.
- [10] a) S. Collins, D. G. Ward, *J. Am. Chem. Soc.* **1992**, 114, 5460; b) K. Soga, H. Deng, T. Yano, T. Shiono, *Macromolecules* **1994**, 27, 7938.
- [11] a) M. Kuroki, T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1987**, 109, 4737; b) M. Kuroki, T. Watanabe, T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1991**, 113, 5903.
- [12] M. Chisholm, *Chem. Br.* **1998**, April, 33.
- [13] In later work, Inoue et al. have shown that thiolate derivatives such as $[\text{Al}(\text{tpp})(\text{SnPr})]$ are active initiators in the absence of a light source: T. Adachi, H. Sugimoto, T. Aida, S. Inoue, *Macromolecules* **1993**, 26, 1238.
- [14] For recent examples, see: a) Cr: A. G. Dosseter, T. F. Jamison, E. N. Jacobsen, *Angew. Chem.* **1999**, 111, 2549; *Angew. Chem. Int. Ed.* **1999**, 38, 2398; b) Al: M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, 120, 5315; c) Co: M. H. Wu, K. B. Hansen, E. N. Jacobsen, *Angew. Chem.* **1999**, 111, 2167; *Angew. Chem. Int. Ed.* **1999**, 38, 1212; d) Cu: L. A. Dakin, S. E. Schaus, E. N. Jacobsen, J. S. Panek, *Tetrahedron Lett.* **1998**, 39, 8947, and references therein.
- [15] T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **1999**, 121, 4072.
- [16] C. P. Radano, G. L. Baker, M. R. Smith, *J. Am. Chem. Soc.* **2000**, 122, 1552.
- [17] a) E. A. Jeffery, A. Meisters, T. Mole, *J. Organomet. Chem.* **1974**, 74, 365; b) E. A. Jeffery, A. Meisters, T. Mole, *J. Organomet. Chem.* **1974**, 74, 373; c) E. A. Jeffery, A. Meisters, T. Mole, *Aust. J. Chem.* **1975**, 28, 801.
- [18] Synthesis and structure of **1**: D. A. Atwood, M. S. Hill, J. A. Jegier, D. Rutherford, *Organometallics* **1997**, 16, 2659.
- [19] Although polymerization can occur at the aluminum center of the MAD activator in the absence of $[\text{Al}(\text{tBu}_4\text{salen})\text{Me}]$ (Table 1, entry 5), the polymerization is only controlled in the presence of the Schiff base complex.
- [20] a) K. Maruyama, T. Ito, A. Yamamoto, *J. Organomet. Chem.* **1978**, 155, 359; b) J. M. Huggins, R. G. Bergman, *J. Am. Chem. Soc.* **1979**, 101, 4410.

Reactive Intermediates on Metal Surfaces: A Ketene Monolayer on Single Crystal Platinum Generated by Photolysis of Pyridyl α -Diazoketones**

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There is considerable current interest in understanding the chemistry of organic molecules as monolayers (saturated layer) on metal surfaces. Much of the effort in this regard has focused on long-chain alkyl thiols or disulfides on gold with

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