A New Class of Alkoxyamines for Efficient
Controlled Homopolymerization of Methacrylates

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Experimental

Materials

Methyl methacrylate (MMA, Quimidroga, technical grade) and styrene (Quimidroga, technical grade) were purified by distillation and were kept at -20 °C until use. Butyl methacrylate (BMA, Aldrich, 99%) was filtered through a column of basic alumina before use. Benzyl bromide (Aldrich, 98%), cyclohexylamine (Aldrich, 99%), tert-butylamine (Aldrich, 98%), chloroacetonitrile (Aldrich, 99%), sodium sulfate (Aldrich, 99%), sodium bicarbonate (Aldrich, 99%), potassium peroxymonosulfate (Oxone®, Aldrich), formalin (37 wt% solution of formaldehyde in water, Aldrich), sodium metabisulfite (Aldrich, 99%), sodium cyanide (Aldrich, 97%), 2,6-Di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy (galvinoxyl, Aldrich) and 2,2’-azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) were used without further purification. Azo-initiator 2,2’-azobis(2-ethylbutyronitrile) (AEBN) was prepared according to Dox J. Am. Chem. Soc. 1925, 47, 1471-7. All other solvents were purchased from Scharlab, were of technical grade, and were used without purification.

Methods

For alkoxyamine syntheses NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer in CDCl₃ as solvent at 298 K or, for fully characterizing alkoxyamines III and IV, in toluene-d₈ at 368 K (because of strong broadening when recorded at ambient temperature). For conversion measurements NMR spectra were recorded on a Bruker Avance DPX 400. The melting points of the synthesized alkoxyamines were determined using a Büchi Melting Point B-450. Molecular weight distributions of polymers were
measured by size exclusion chromatography (SEC). Samples were dried and diluted in THF (HPLC grade) to a concentration of approximately 5 mg.ml\(^{-1}\) and filtered through a 0.45-µm nylon filter. The SEC set up consisted of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6 with pore sizes ranging from 10\(^2\) to 10\(^6\) Å). Chromatograms were obtained in THF (HPLC grade) at 35 °C using a flow rate of 1 ml.min\(^{-1}\). The equipment was calibrated using narrow MWD polystyrene standards ranging from 595 to 3.95 × 10\(^6\) Da (5\(^{th}\) order universal calibration). UV measurements were recorded on a Shimadzu UV-2550 spectrometer.

**Alkoxyamine Synthesis**

(Z)-N-(Cyanomethylene)-2-methylpropan-2-amine Oxide.

![Chemical structure](image)

Step 1: Into a 500-mL Erlenmeyer flask with stirrer bar were charged 252 mL (3 equiv) of tert-butylamine and 150 mL of tetrahydrofuran and the flask was cooled in a water bath. To this was added drop wise 60.4 g (50.6 mL, 0.8 mol) of chloroacetonitrile in ca. 30 min and the resulting mixture was left to stand for 3 days at room temperature. The reaction mixture was then filtered with the aid of 250 mL of ethyl acetate. The filtrate was washed with water, brine, dried over sodium sulfate, and after filtration the volatiles were evaporated to yield 73.6 g (82%) of a colorless liquid of greater than 98% purity (\(^1\)H NMR) and suited as such for further use. \(^1\)H NMR \(\delta\) 1.11 (s, 9 H, \(t\)-Bu), 1.17 (br, 1 H, N-H), 3.53 (s, 2 H, CH\(_2\)); \(^13\)C NMR \(\delta\) 28.91 (\(t\)-Bu), 31.17 (CH\(_2\)), 51.51 (C-N), 119.90 (C=\(N\)).
Step 2: The product of Step 1 dissolved in 450 mL of acetone was added to a 2-L beaker containing a mechanically stirred solution/suspension of 250 g of sodium bicarbonate in 450 mL of water. 460 g of Oxone® (1.13 mole equiv) was added in small portions of ca. 10 g over the course of 1 h; small portions of crushed ice were occasionally added to maintain the reaction temperature below ca. 40 °C. After Oxone® addition was complete, stirring was continued for 1 h. Next, 400 mL of ethyl acetate was added, and after stirring for 5 min the mixture was allowed to phase separate, where after the top layer was decanted; this was repeated 3 times with 200 mL portions each of ethyl acetate. The combined organic phases were washed twice with brine, dried over sodium sulfate, and after filtration the solvents were evaporated to leave a reddish liquid that may crystallize on standing. Yield 70.6 g (85%, or 70% over 2 steps). The product is sufficiently pure for further use. $^1$H NMR $\delta$ 1.54 (s, 9 H, t-Bu), 6.85 (s, 1 H, HC=N); $^{13}$C NMR $\delta$ 28.16 (t-Bu), 74.78 (C-N), 103.88 (C=N), 112.98 (C≡N).

Alkoxyamine I 3-(tert-Butyl(2-cyanopropan-2-yloxy)amino)-2,2-dimethylsuccinonitrile.

18.92 g (0.15 mol) of (Z)-N-(cyanomethylene)-2-methylpropan-2-amine oxide and 40.64 g (1.6 equiv) of AIBN in 250 mL of toluene were stirred at 92 °C (bath temp) for 6 h. By evaporation of the solvent, then recrystallization from isopropanol and cooling in a refrigerator, ca. 80% of the alkoxyamine was recovered, contaminated by 10-20% tetramethylsuccinimide (TMSN). When this material was dissolved in hot isopropanol and
the solution slowly cooled to room temperature, pure alkoxyamine was obtained. Yield:
26.0 g (66%). $^1$H NMR $\delta$ 1.26 (s, 9 H, $t$-Bu), 1.50, 1.61, 1.82 and 1.82 (each s, 3 H, Me),
3.77 (s, 1 H, CH-N); $^{13}$C NMR $\delta$ 24.51, 26.13, 28.18 and 28.18 (each Me), 26.61 ($t$-Bu),
36.25 ($CMe_2$), 61.98 (CH-N), 63.08 (C-N), 76.58 (C-O), 113.46, 121.09 and 122.12 (each
C≡N); Melting point range: 141-144 °C; High resolution MS-ES calc. for $C_{14}H_{22}N_4ONa$ [M

*Alkoxyamine II 3-(tert-Butyl(3-cyanopentan-3-yloxy)amino)-2,2-diethylsuccinonitrile.*

5.68 g (45 mmol) of (Z)-$N$-(cyanomethylene)-2-methylpropan-2-amine oxide and 15.86 g
(1.6 equiv) of AEBN in 75 mL of toluene were stirred at 86 °C (bath temp) overnight.
NMR analysis indicated that conversion was close to 90%; beside the desired alkoxyamine
as the main component small amounts of presumably nitroxide ($\delta$ 4.20) and of NOH
compound, 3-(tert-butyl(hydroxy)amino)-2,2-diethylsuccinonitrile ($\delta$ 5.43 (br, NOH) and
3.90 (CH-N)), formed by disproportionation were present. Evaporation of solvent, then
recrystallization from isopropanol and cooling in a freezer, gave after filtration 5.40 g
(38%) of alkoxyamine as needles. $^1$H NMR $\delta$ 1.06, 1.11, 1.13 and 1.18 (each t, 3 H,
$CH_3CH_2$), 1.28 (s, 9 H, $t$-Bu), 1.55 (m, 1 H), 1.86-2.15 (m, 5 H) and 2.18-2.34 (m, 2 H)
($CH_3CH_2$), 4.04 (s, 1 H, CH-N); $^{13}$C NMR $\delta$ 7.92, 8.28, 8.93 and 9.13 (each $CH_3CH_2$),
25.28, 28.24, 29.32 and 30.64 (each $CH_3CH_2$), 26.98 ($t$-Bu), 45.38 ($CEt_2$), 58.70 (CH-N),
63.88 (C-N), 84.50 (C-O), 113.96, 119.45 and 120.64 (each C≡N). Melting point range: 81-83 °C; High resolution MS-ES calc. for C_{18}H_{30}N_{4}ONa [M + Na]^+: 341.2317; found: 341.2319.

(Z)-N-(Cyanomethylene)cyclohexanamine Oxide.

Step 1: To a solution of 125.3 g (0.66 mol) of sodium metabisulfite in 200 mL of water was added 97.4 g of ≥37% formalin (≥ 1.2 mol) (caution: exothermic) and the solution was heated for 45 min at 70 °C. After cooling to 60 °C, 126.0 g (1.27 mol) of cyclohexylamine was rapidly added and stirring was continued for 0.5 h at that temperature. After cooling to room temperature, a solution of 62.5 g (1.275 mol) of sodium cyanide in 250 mL of water was added drop wise in 1 h, and stirring was continued for 4 h. Water and toluene (500 mL each) were added and the layers were separated. The aqueous layer was extracted once more with 250 mL of toluene. The combined organic layers were washed with water and with brine, dried over sodium sulfate, and after filtration the solvents were evaporated to give 155.9 (94%) of the product as a colorless liquid that is sufficiently pure for the next step. It contains less than 2% of bis-alkylation product (δ 3.67). $^1$H NMR δ 0.99-1.34 (m, 6 H) and 1.54-1.85 (m, 5 H) (c-Hex and N-H), 2.64 (tt, 1 H, CH-N), 3.58 (s, 2 H, CH$_2$CN); $^{13}$C NMR δ 24.59, 26.05, 32.77 and 34.49 (c-Hex), 55.32 (CH$_2$CN), 118.30 (C≡N).

Step 2: according to the general recipe described in the first example with a slightly higher excess of sodium bicarbonate and Oxone®: using the crude product of Step 1 and 465 g of sodium bicarbonate in 600 mL each of acetone and water, then adding portion
wise 850 g of Oxone® in 2 h. Recrystallization from n-heptane-ethyl acetate (3:1 v/v) gave a first crop of nitrone. Evaporation of the filtrate followed by recrystallization gave a second crop. Total yield: 126.2 g (75%) of (Z)-nitrone, containing typically less than 5% (E)-isomer (δ 6.64). \( ^1H \) NMR δ 1.13-1.36 (m, 3 H) and 1.60-2.04 (m, 7 H) (c-Hex), 3.92 (tt, 1 H, CH-N), 6.79 (s, 1 H, HC=N); \( ^{13}C \) NMR δ 24.71, 24.75 and 31.25 (c-Hex), 76.53 (CH-N), 105.26 (HC=N), 112.66 (C≡N).

**Alkoxyamine III** 3-(((2-Cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethylsuccinonitrile.

45.66 g (0.3 mol) of (Z)-N-(cyanomethylene)cyclohexanamine oxide and 81.3 g (1.65 equiv) of AIBN in 600 mL of isopropanol were stirred for 6 h at 92 °C (oil bath temperature). Heating and stirring were switched off, and the mixture was allowed to slowly cool to room temperature. The crystals were filtered on a Büchner funnel, washed with isopropanol and air dried. Yield: 76.15 g (88%) of pure alkoxyamine as white crystals. \( ^1H \) NMR δ 0.85-1.75 (m, 9 H) and 2.45 (m, 1 H) (c-Hex), 1.19, 1.20, 1.28 and 1.38 (each s, 3 H, Me), 3.36 (br tt, 1 H, CH-N c-Hex), 3.54 (br s, 1 H , CH-N); \( ^{13}C \) NMR δ 24.92, 25.85, 26.03, 26.03, 26.30, 26.45, 27.08, 27.58 and 32.87 (c-Hex and 4 Me), 36.25 (C\( \text{Me}_2 \)), 63.07 and 65.77 (each CH-N), 73.60 (C-O), 114.86, 121.55 and 121.6 (each C≡N); Melting point
range: 130-132°C; High resolution MS-ES calc. for C_{16}H_{25}N_{4}O [M + H]^+ : 289.2028; found: 289.2040.

(Z)-N-Benzylidenecyclohexanamine Oxide.

Step 1: into a 1-L Erlenmeyer flask with stirrer bar were charged 320 mL (3.5 equiv) of cyclohexylamine and 600 mL of ethyl acetate and the solution was cooled in an ice bath. To the stirred solution was added drop wise 136.8 g (95.1 mL; 0.8 mol) of benzyl bromide in ca. 1 h and the resulting mixture was stirred overnight at room temperature. The reaction mixture was filtered with the aid of 250 mL of toluene. The filtrate was washed with water and with brine, dried over sodium sulfate, and after filtration the volatiles were evaporated. Residual cyclohexylamine was removed by co-evaporation with toluene. This gave 186.6 g (98%) of product as a colorless liquid that was sufficiently pure for the next step. It contained less than 3% of bis-alkylation product (δ3.60). ^1H NMR δ 1.01-1.32 (m, 6 H) and 1.53-1.93 (m, 5 H) (c-Hex and N-H), 2.46 (tt, 1 H, CH-N), 3.78 (s, 2 H, CH$_2$Ph), 7.20-7.55 (m, 5H, Ph); ^13C NMR δ 25.19, 26.40 and 33.77 (c-Hex), 51.25 (CH-N), 56.36 (CH$_2$Ph), 126.96, 128.23 and 128.52 (C-H, Ph), 141.23 (q-C, Ph).

Step 2: according to the general recipe described in the first example using the crude product of Step 1 and 300 g of sodium bicarbonate in 500 mL each of acetone and water, then adding portion wise 530 g of Oxone® gave crude nitrone in nearly quantitative yield.
Recrystallization from *n*-heptane-ethyl acetate (7:1 v/v) gave a first crop. Evaporation of the filtrate followed by recrystallization gave a second crop. Total yield: 132.5 g (85%) of nitrone as a single isomer. $^1$H NMR $\delta$ 1.11-1.39 (m, 3 H), 1.60 (m, 1 H) and 1.83-2.12 (m, 6 H) (c-Hex), 3.79 (tt, 1 H, CH-N), 7.28-7.38 (m, 3 H, Ph), 7.38 (s, 1 H, HC=N), 8.21 (m, 2 H, Ph); $^{13}$C NMR $\delta$ 25.12, 25.12 and 31.22 (c-Hex), 75.69 (CH-N), 128.48, 128.59 and 130.06 (C-H, Ph), 130.95 (q-C, Ph), 132.19 (HC=N).

**Alkoxyamine IV** 3-(((2-Cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile.

24.39 g (0.12 mol) of (Z)-N-benzyldene-cyclohexanamine oxide and 32.51 g (1.65 equiv) of AIBN in 250 mL of toluene were stirred at 92 °C (bath temp) for 6 h. Evaporation of the solvent, re-dissolving the product in hot isopropanol and slowly cooling to room temperature, afforded a first crop. Evaporation of the filtrate and recrystallization from methanol afforded a second. Total yield: 29.44 g (72%) of crystalline alkoxyamine. $^1$H NMR $\delta$ 0.74-1.75 (m, 10 H, c-Hex), 0.91, 1.38, 1.49 and 1.57 (each s, 3 H, Me), 3.54 (tt, 1 H, CH-N c-Hex), 3.5-4.2 (br, 1 H, PhCH), 7.03-7.14 (m, 3 H) and 7.55-7.65 (m, 2 H) (Ph); $^{13}$C NMR $\delta$ 26.39, 26.47, 26.71, 26.81, 27.26, 27.39, 28.32 (br), 29.31 and 34.03 (br) (each C-H, c-Hex and 4 Me), 35.53 (CMe$_2$), 63.69 (C-H, c-Hex), 72.37 (C-O), 72.25 (br, PhCH), 122.47 and 124.84 (each C=N), 128.40, 128.54 and 131.13 (each C-H, Ph), 136.97 (br q-C, Ph);
Melting point range: 136-138°C; High resolution MS-ES calc. for C_{21}H_{30}N_{3}O [M + H]^+ : 340.2389; found: 340.2394.

*Methyl 3-(tert-butyl(1-methoxy-2-methyl-1-oxopropan-2-yloxy)amino)-3-cyano-2,2-dimethylpropanoate.*

Procedure A. 5.68 g (45 mmol) of (Z)-N-(cyanomethylene)-2-methylpropan-2-amine oxide and 12.95 g (1.25 equiv) of dimethyl 2,2'-azobis(isobutyrate) (AIBMe) in 75 mL of toluene were stirred at 92 °C (bath temp) for 6 h. The final conversion amounted to 92% of the nitrone, 75% being the desired alkoxyamine and 17% consisting of a 1:1 mixture of 2-(tert-butyl)-4,4-dimethyl-5-oxoisoxazolidine-3-carbonitrile (δ 4.06: s, 1 H, H-3) – formed by disproportionation of alkoxyamine to NOH compound followed by cyclization – and methyl 2-(tert-butyl)-3-cyano-5-methylisoxazolidine-5-carboxylate (2.48, 3.20 and 3.96: each dd, 1 H, H-3 and H-4), formed by cycloaddition of starting nitrone to methyl methacrylate formed in the disproportionation. Isolation was not attempted.

Procedure B using Atom Transfer Radical Addition (ATRA). To 7.57 g (60 mmol) of (Z)-N-(cyanomethylene)-2-methylpropan-2-amine oxide and 30.2 g (2.9 equiv) of
pentamethyldiethylenetriamine in 100 mL of nitrogen-flushed methanol was added a mixture of 16.25 g of copper(I) bromide and 2.70 g of copper powder (2.6 equiv of copper). To the stirred solution was added at room temperature in 0.5 h a solution of 27.15 g (2.5 equiv) of methyl α-bromoisobutyrate in 20 mL of nitrogen flushed methanol and the reaction was stirred overnight, when starting nitrone had been completely converted. The reaction was poured into 250 mL of 50%-saturated aqueous ammonium chloride and 250 mL of dichloromethane was added. After separation the water was extracted twice with 125-mL portions of dichloromethane. The combined organic fractions were washed twice with 50%-saturated aqueous ammonium chloride, once with brine, dried over sodium sulfate, and after filtration solvents were removed in vacuum. The product was purified by flash column chromatography, followed by recrystallization from isopropanol to give a first crop of pure alkoxyamine. The filtrate was evaporated and again recrystallized from isopropanol to give a second crop. Combined yield: 12.62 g (64%) of white crystals. $^1$H NMR $\delta$ 1.11 (s, 9 H, tJBu), 1.28 (s, 6 H), 1.46 (s, 3 H) and 1.49 (s, 3H) (each Me), 3.66 and 3.68 (each s, 3 H, OMe), 4.28 (s, 1 H, CH-N); $^{13}$C NMR $\delta$ 21.77, 23.88, 24.28 and 24.45 (each Me), 26.46 (t-Bu), 46.61 (CMe$_2$), 51.77 and 52.12 (each OMe), 61.29 (CH-N), 62.82 (C-N), 78.68 (C-O), 115.80 (C≡N), 174.57 and 175.19 (each C=O). Attempted polymerization of methyl methacrylate using this alkoxyamine resulted in uncontrolled polymerization with a limiting conversion of <70% (see Figure S1) and a static molecular weight of $M_n \approx 5000$ g/mol.

**Nitroxide-Mediated Polymerization**
Nitrooxide-mediated polymerizations were carried out in solution in a 25-mL round bottom flask. In a typical reaction, methyl methacrylate (5 g, 50 mmol) was added to toluene (5 g) containing the alkoxyamine initiator, 3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (163 mg, 0.5 mmol), and the oxygen was removed by continuous nitrogen bubbling for 1 hour. The reaction mixture was heated to 90 °C in an oil bath with continuous stirring and left for 5 h. At regular time intervals, a sample of 0.1 ml was removed and diluted to 0.7 ml with CDCl$_3$ and the NMR spectrum was recorded. Fractional conversion, $X$, was measured by NMR by comparison of the integral of the vinyl protons at 5.6 and 6.2 ppm to the combined signal of the OCH$_3$ signals from both monomer and polymer at 3.8 ppm and 3.7 ppm. Similarly, at the same time intervals, 0.1 ml of the reaction mixture removed and dried in air. The resulting solid was dissolved in 5 ml THF in order to perform the SEC measurements. After 6 h the polymer solution was precipitated in ice cold MeOH and the polymer was obtained by filtration and vacuum dried ($X = 0.68$, $M_n = 8100$ g.mol$^{-1}$, $D = 1.49$).

**Block Copolymer Synthesis**

To 500 mg of pMMA homopolymer (see above) was added 1 g of butyl methacrylate. After stirring at room temperature until the polymer had dissolved completely, oxygen was removed by continuous nitrogen bubbling for 1 hour. The reaction mixture was heated to 90 °C in an oil bath with continuous stirring and left for 4 h at which point the conversion was measured by NMR and the polymer was precipitated in MeOH and the polymer was obtained by filtration and vacuum dried ($X = 0.35$, $M_n = 19800$ g.mol$^{-1}$, $D = 1.46$).
An additional experiment was conducted using a pMMA macroinitiator synthesized at 96 °C. MMA (5 g), toluene (5 g) and 3-((((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (169 mg) were deoxygenated by purging with N₂ and the reaction mixture was placed in an oil bath at 96 °C. After 4 h the polymer solution was diluted with THF, then precipitated in ice cold MeOH and the polymer was obtained by filtration and vacuum dried (X = 0.72, $M_n = 11000 \text{ g.mol}^{-1}$, $D = 1.29$). The pMMA homopolymer (777 mg) was dissolved in a mixture of butyl methacrylate (3 g) and toluene (3 g). The reaction was heated to 94 °C for overnight at which point the polymer was precipitated in ice cold MeOH and the polymer was obtained by filtration and vacuum dried (X=0.20, $M_n = 18000 \text{ g.mol}^{-1}$, $D = 1.25$) (see Figure S8).

Online NMR experiments

Alkoxyamine IV (17 mg, 0.05 mmol) was dissolved in a mixture of methyl methacrylate (0.5 g, 5 mmol) and toluene-d₈. The mixture was transferred into a NMR tube equipped with a Young valve. Oxygen was removed by bubbling with nitrogen and the tube was sealed and stored in an ice bath until it was added to the preheated spectrometer at 90 °C. $^1$H NMR spectra were recorded every 10 minutes for 800 minutes.

Measurement of $k_d$

The rate coefficient of decomposition of the various alkoxyamines was measured by radical trapping experiments using galvinoxyl. $p$-Xylene (2 ml) was placed in a quartz cuvette and nitrogen was bubbled through for 5 minutes. The cuvette was sealed with a rubber septum and heated to the desired temperature within a temperature control unit. The temperature was left to equilibrate for 20 minutes and 175 µl of 1mM solution of galvinoxyl in xylene
was injected via syringe. Then, 175 µl of a 1mM solution of alkoxyamine was injected via syringe. The UV absorbance at 407 nm was measured continuously. The rate coefficient was calculated by plotting the change in absorbance A with time according to

\[-\ln\left(\frac{A}{A_0}\right) = k_d t\]

The measurements were repeated at 50, 60 and 70 °C in order to yield the Arrhenius parameters.
**Figure S1** Evolution of conversion with time (left) and evolution of $M_n$ with conversion (right) for polymerization of methyl methacrylate with [MMA]/[Alkoxyamine] = 100 using methyl 3-(tert-butyl(1-methoxy-2-methyl-1-oxopropan-2-yloxy)amino)-3-cyano-2,2-dimethylpropanoate at 90 °C as 50 wt% solution in toluene.
Figure S2 Evolution of molecular weight and dispersity for polymerization of methyl methacrylate for alkoxyamine IV with [MMA]/[Alkoxyamine] = 100 (filled squares), [MMA]/[Alkoxyamine] = 200 (filled circles) and [MMA]/[Alkoxyamine] = 400 (filled triangles).
Figure S3 Decomposition of alkoxyamines by radical trapping experiments with Galvinoxyl at 70 °C. Blocbuilder (black squares), alkoxyamine IV terminated poly(methyl methacrylate) (blue triangles), alkoxyamine II (pink triangles), alkoxyamine I (green triangles), alkoxyamine IV (red circles), alkoxyamine III (gold triangles).
Table S1 Arrhenius parameters and value of decomposition rate coefficient at 90 °C for various alkoxyamines.a

<table>
<thead>
<tr>
<th>Alkoxyamine</th>
<th>A (s⁻¹)</th>
<th>Ea (kJ.mol⁻¹)</th>
<th>$k_{d,90}$ (s⁻¹)b</th>
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<tr>
<td>Blocbuilder</td>
<td>$4.3 \times 10^{14}$</td>
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<tr>
<td>I</td>
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<td>115</td>
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<td>$6.6 \times 10^{13}$</td>
<td>109</td>
<td>0.014</td>
</tr>
</tbody>
</table>

a Due to the very slow decomposition of alkoxyamine III at low temperatures the values for $k_d$ at temperatures lower than 70 °C could not be obtained and therefore the Arrhenius parameters are not included. At higher temperatures the decomposition of galvinoxyl can affect the accurate measurement of $k_d$ by the present method.

bRate coefficient for alkoxyamine decomposition at 90 °C estimated from the Arrhenius parameters.
Figure S4 Evolution of $^1$H NMR spectra during the polymerization of methyl methacrylate as 50 wt% solution in toluene-$d_8$ in the presence of alkoxyamine IV ([M]$_0$/[IV]=100).
Figure S5 Evolution of $^1$H NMR spectra during the polymerization of methyl methacrylate as 50 wt% solution in toluene-d$_8$ in the presence of alkoxyamine IV ([M]$_0$/[IV]=100) showing the disappearance of an the cyanoisopropyl group from the initiating moiety.
Figure S6 Evolution of $^1$H NMR spectra during the polymerization of methyl methacrylate as 50 wt% solution in toluene-d$_8$ in the presence of alkoxyamine IV ([M]$_0$/[IV]=100) showing the appearance of an unsaturated peak at high conversions (highlighted).
**Figure S7** $^1$H NMR spectrum of poly(methyl methacrylate) produced using alkoxyamine IV after precipitation. Inset shows the region in which signal arising from terminal unsaturations would occur.
Figure S8 Molecular weight distribution of poly(methyl methacrylate) initiated by alkoxyamine IV with [MMA] / [Alkoxyamine] = 100 (blue) at 96 °C and molecular weight distribution after chain extension with butyl methacrylate (red).
Figure S9 Evolution of conversion, molecular weight and dispersity (measured by SEC-MALLS) for polymerization of styrene for alkoxyamine IV with [Styrene]/[Alkoxyamine] = 333 conducted at 75 wt% in tert-butyl benzene at 126 °C.