

Supporting Information

Nitroxide Mediated Polymerization of methacrylates at moderate temperature

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Materials. Methyl methacrylate (MMA, >99%, Aldrich), benzyl methacrylate (BzMA, Aldrich), trifluoroethyl methacrylate (TFMA, Aldrich), 2-dimethylaminoethyl methacrylate (DMAEMA, Aldrich), styrene (St, Aldrich) and n-butyl acrylate (nBuA, Aldrich) were dried over calcium hydride, degassed by several freeze-thawing cycles before being distilled under reduced pressure and stored under argon. 2-hydroxyethyl methacrylate (HEMA, Aldrich) was used as received and degassed by bubbling argon for 30 min before use. 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) (96%, Wako) was stored at -20°C and used as received. Methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) was synthesized according to literature¹ and stored at -20°C (degradation of this compound has been observed when stored in a fridge at 4°C for a few weeks).

Characterizations. Monomer conversions were determined by ¹H NMR spectroscopy at 298 K with a Bruker spectrometer operating at 400 MHz in CDCl₃. The molecular weights (M_n) and polydispersity indices (M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) (flow rate: 1 mL/min) at 40°C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5 μm, 10⁵ Å, 10⁴ Å, 10³ Å, and 10² Å). Poly(methyl methacrylate) (PMMA) standards were used for calibration. Mass spectrometry analyses on the PMMA product were performed on a Waters QToF2 mass spectrometer. The analyte solutions (1 mg/mL) were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 μL/min. Typical ESI conditions were: capillary voltage, 3.1 kV; cone voltage, 30 V; source temperature, 80 °C; desolvation temperature, 120°C; 8 mbar pressure between extraction cone and sample cone. Following a custom-made modifications of the ion source of the QToF instrument, the pressure in the transmission region that is defined by the volume between the sample cone and the extractor cone is measured by a Pirani ion gauge. Regular pressure, i.e. at full pumping speed, is at 1,2 mbar.²

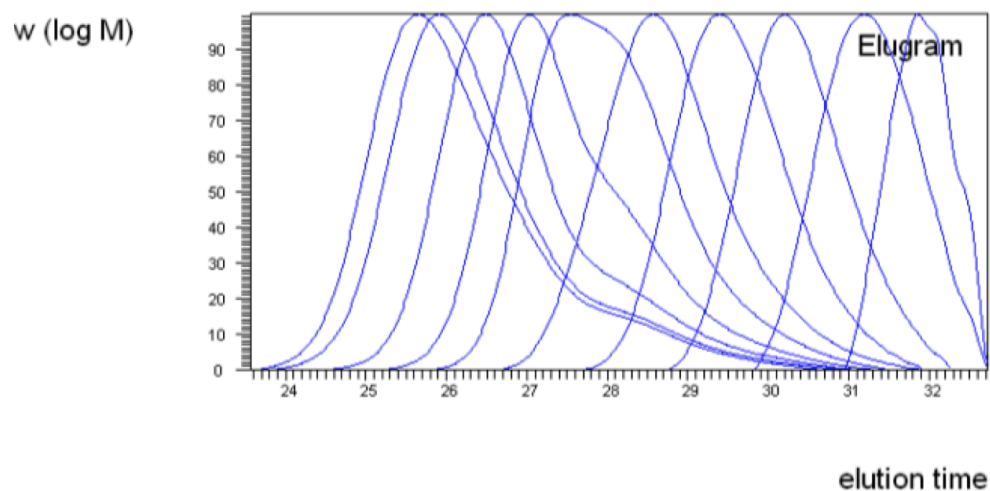
Dry nitrogen was used as the ESI gas. For the recording of the single-stage ESI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from *m/z* 50 to 2500, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. For the ESI-MSMS experiments, the ions of interest were mass-selected by the quadrupole mass filter. The precursor ion resolution was adjusted to select only the monoisotopic signal. The selected ions were then submitted to collision against argon in the rf-only hexapole collision cell (pressure estimated at 0.9 - 1 mBar). The laboratory frame kinetic energy (ELab), typically at 50 eV, was selected to afford intense enough fragment ion signals. All ions coming out of the hexapole cell, either the fragment or the undissociated precursor ions, were finally mass measured with the oa-ToF analyser. Data were acquired in continuum mode until acceptable average data were obtained.

EPR studies were carried out with a Miniscope MS400 (Magnetech, Berlin, Germany) benchtop spectrometer working at X-band with a modulation amplitude of 2G, a sweep width of 68G, a sweep time of 30 s, and a microwave power of 10mW. The temperature was adjusted with the temperature controlled unit TC H03 (Magnetech), providing an electronic adjustment in steps of 0.1°C in the range of -170°C to 250°C. The solutions were ramp heated to 50°C for the ESR measurements.

Typical polymerization procedure. In a 50 ml one-necked round bottom flask fitted with a three-way stopcock connected to either a nitrogen line or a vacuum pump, 0.12 g NMMA (0.68 mmol) and 0.21 g V70 (0.68 mmol) were added. Oxygen was removed from the reaction flask by repeated vacuum-argon cycles and finally filled with argon. Then, 20 ml of degassed MMA (0.187 mol) were added to the flask. The flask was then immersed in an oil bath thermostated at 50°C. Samples were regularly withdrawn from the polymerization medium for the determination of the conversion by ¹H NMR analysis and for the molecular weight and polydispersity determinations by SEC analysis. Results are summarized in Figures 1 and 2.

PMMA used for the resumption experiments (Figure 2 and S6) are further purified to remove unreacted monomer, V70 and NMMA. For that purpose, PMMA is dissolved in THF and precipitated 3 times in heptane prior to drying under vacuum at 30°C for 24h.

a)



b)

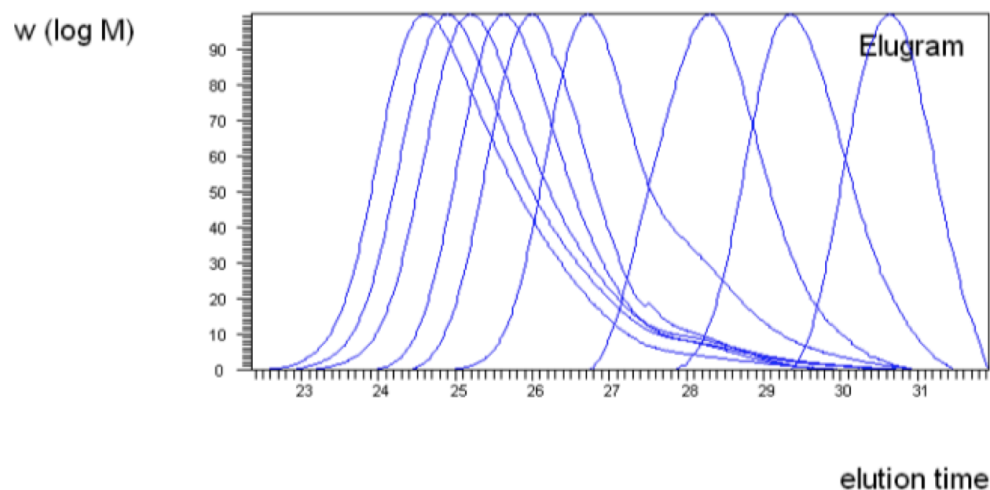


Figure S1. SEC chromatogram evolutions for the methyl methacrylate polymerization initiated by V70 in the presence of NMMA at 50°C. a) $[MMA]/[V70]/[NMMA] = 275/1/1$, bulk; b) $[MMA]/[V70]/[NMMA] = 550/1/1$, bulk. See Figure 1 and S2 for the molar masses, molar mass distributions and kinetics of this polymerization.

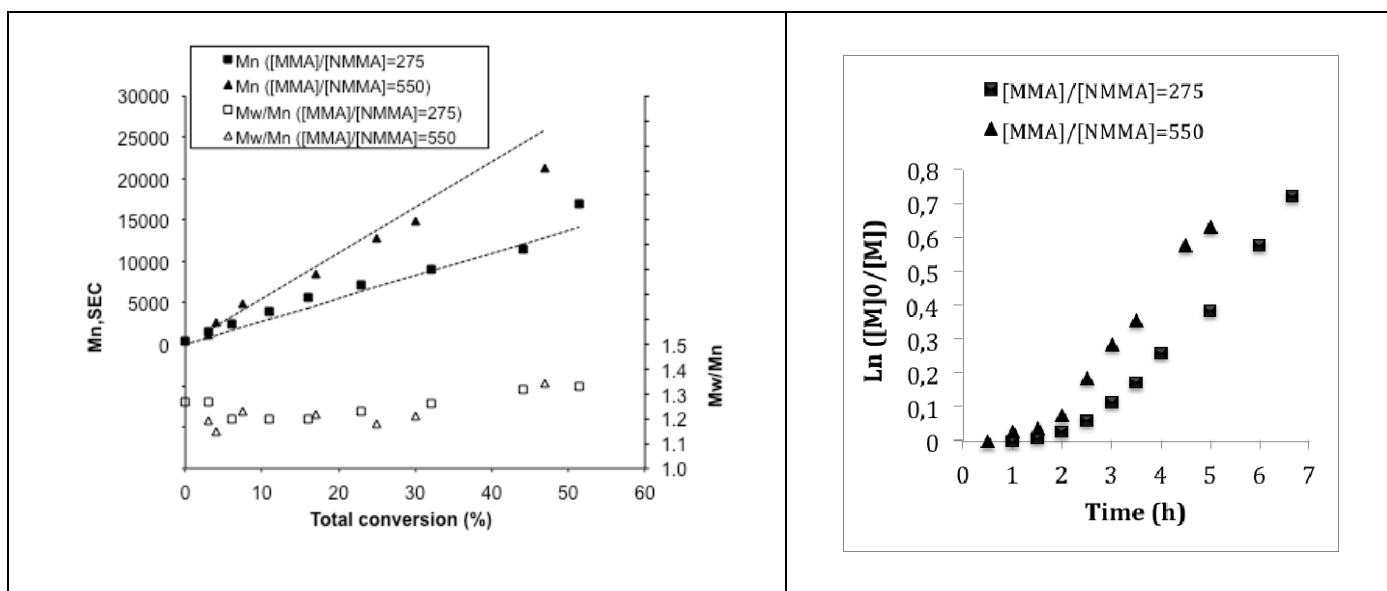


Figure S2. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the methyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different $[MMA]/[NMMA]$ ratios (squares: 275, triangles: 550). Conditions: squares: $[MMA]/[V70]/[NMMA] = 275/1/1$, bulk; triangles: $[MMA]/[V70]/[NMMA] = 550/1/1$, bulk; $Mn_{th} = ([MMA]_0/[alkoxyamine]_{th}) \times Mr(MMA) \times \text{conversion}$; where $[MMA]_0$ is the initial MMA concentration, $Mr(MMA)$ is the molecular weight of MMA and $[alkoxyamine]_{th}$ is the theoretical concentration of alkoxyamine

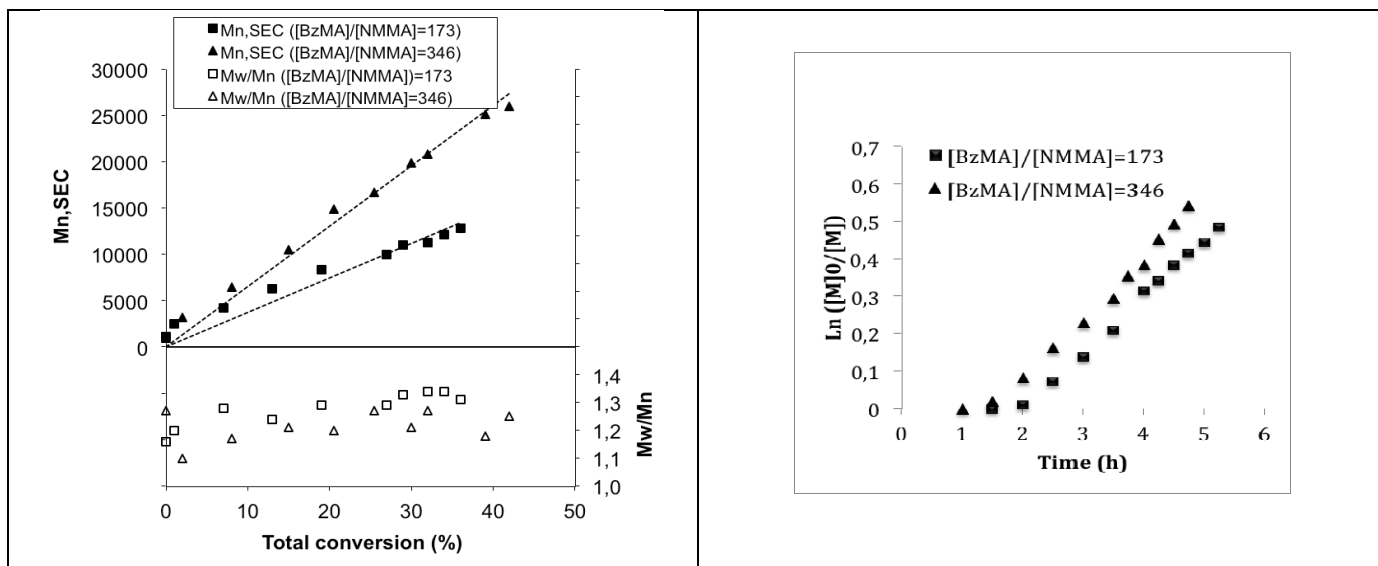


Figure S3. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the benzyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different $[BzMA]/[NMMA]$ ratios (squares: 173, triangles: 346). Conditions: squares: $[BzMA]/[V70]/[NMMA] = 173/1/1$, bulk; triangles: $[BzMA]/[V70]/[NMMA] = 346/1/1$, bulk. Dotted lines are regression lines.

a)

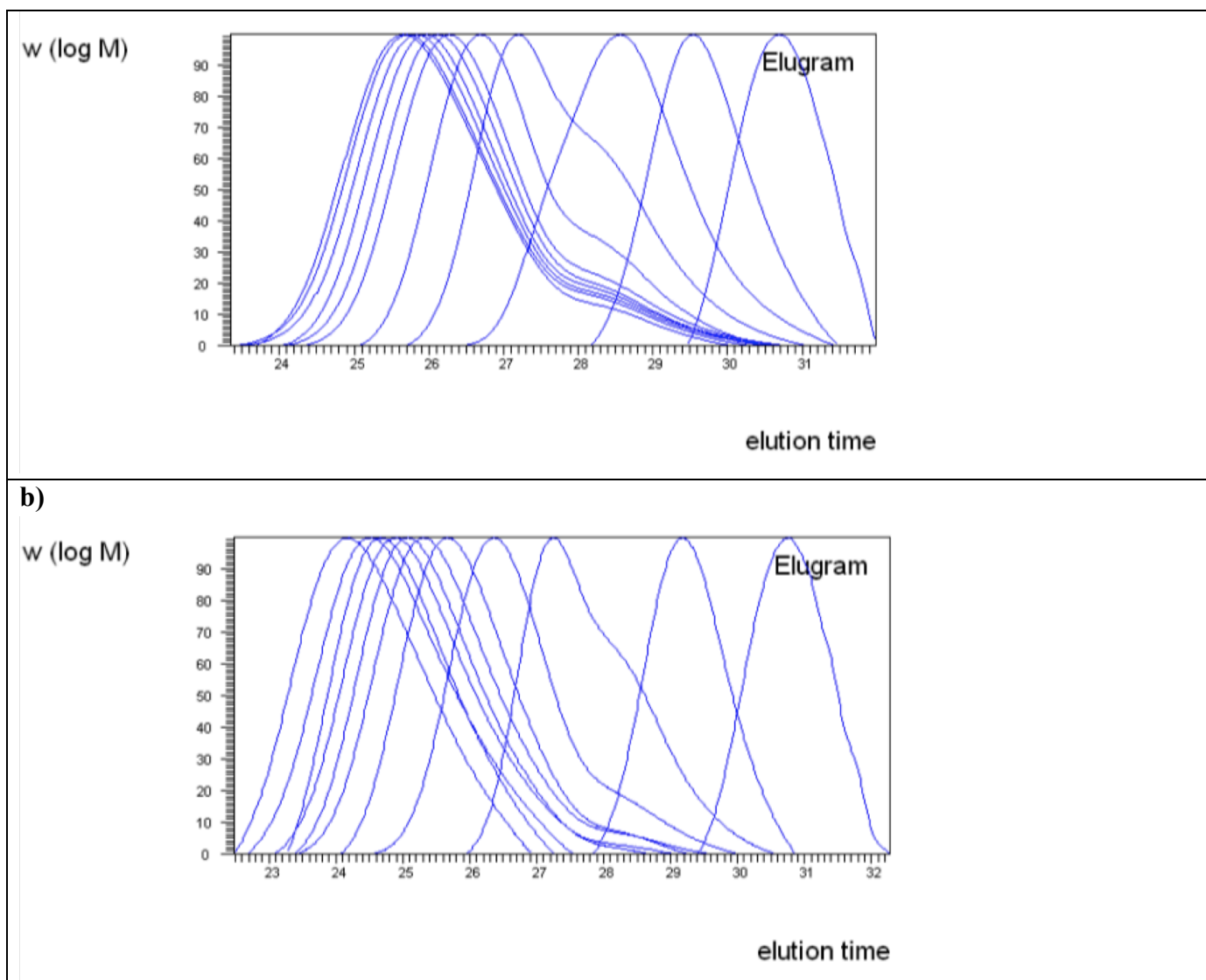


Figure S4. SEC chromatogram evolutions for benzyl methacrylate polymerization initiated by V70 in the presence of NMMA at 50°C. a) $[BzMA]/[V70]/[NMMA] = 173/1/1$, bulk; b) $[BzMA]/[V70]/[NMMA] = 346/1/1$, bulk. See Figure S3 for the molar masses, molar mass distributions and kinetics of this polymerization

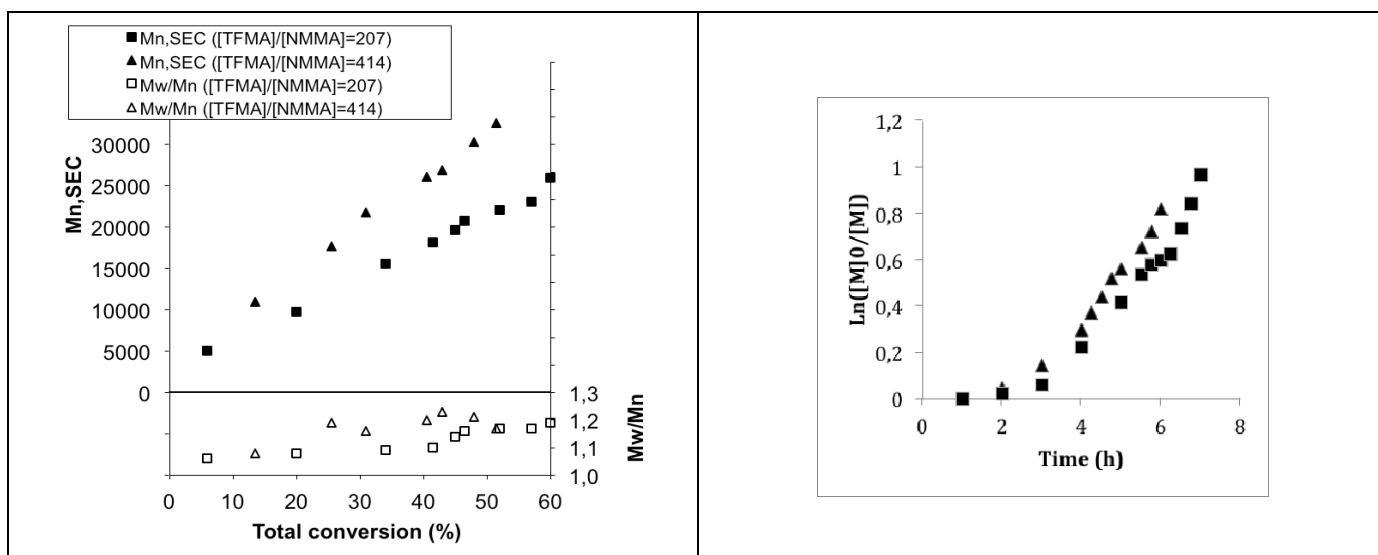


Figure S5. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the trifluoroethyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different [TFMA]/[NMMA] ratios (squares: 207, triangles: 414). Conditions: squares: [TFMA]/[V70]/[NMMA] = 207/1/1, bulk; triangles: [TFMA]/[V70]/[NMMA] = 414/1/1, bulk. Dotted lines are regression lines.

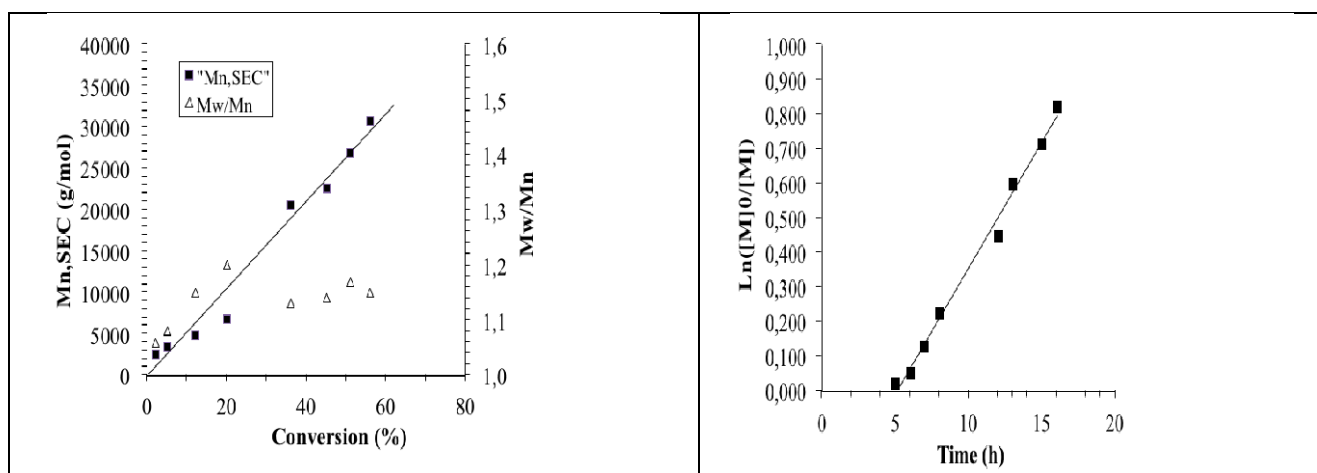


Figure S6. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the trifluoroethyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 40°C. Conditions: squares: [TFMA]/[V70]/[NMMA] = 207/1/1, bulk. Solid line: regression line.

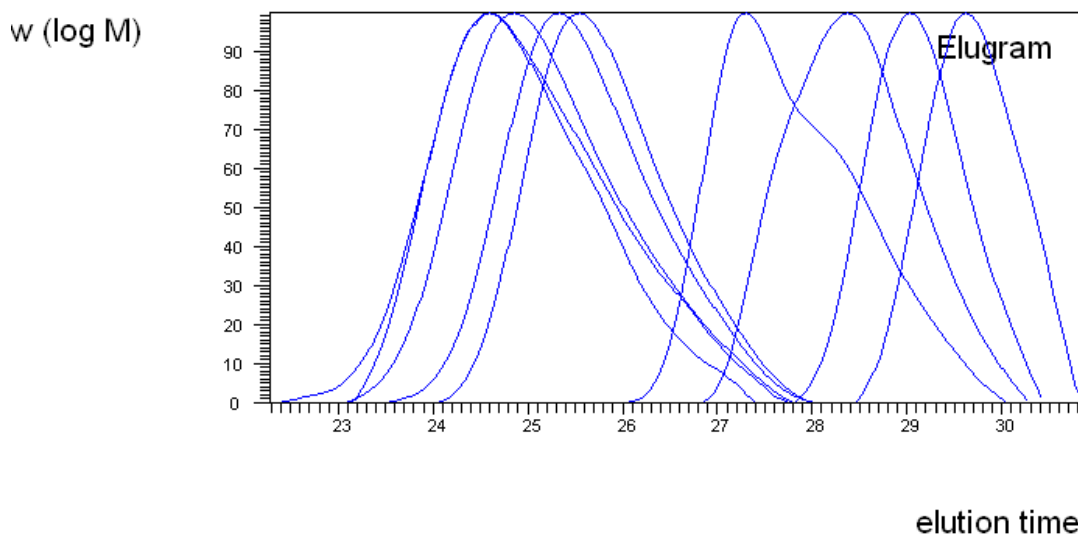


Figure S7. SEC chromatogram evolutions for trifluoroethyl methacrylate initiated by V70 in the presence of NMMA at 40°C. Conditions: [TFMA]/[V70]/[NMMA] = 207/1/1, bulk. See Figure S6 for the molar masses, molar mass distributions and kinetics of this polymerization.

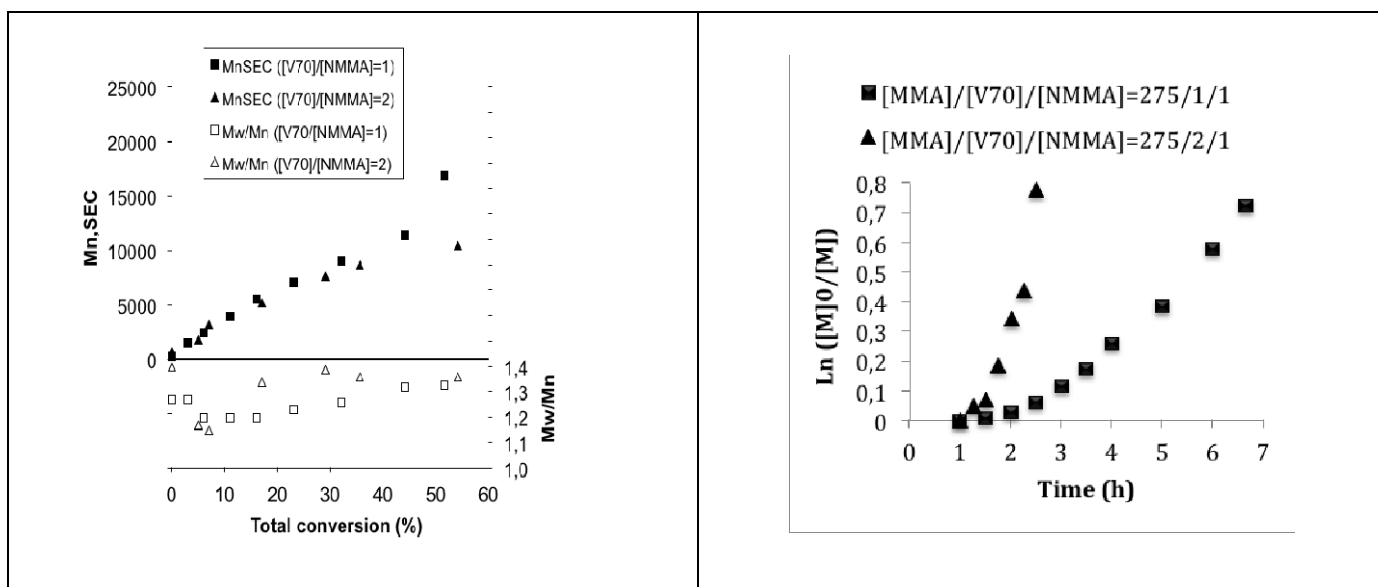


Figure S8. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the methyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different [V70]/[NMMA] ratios. Conditions: squares: [MMA]/[V70]/[NMMA] = 275/1/1, bulk; triangles: [MMA]/[V70]/[NMMA] = 275/2/1, bulk.

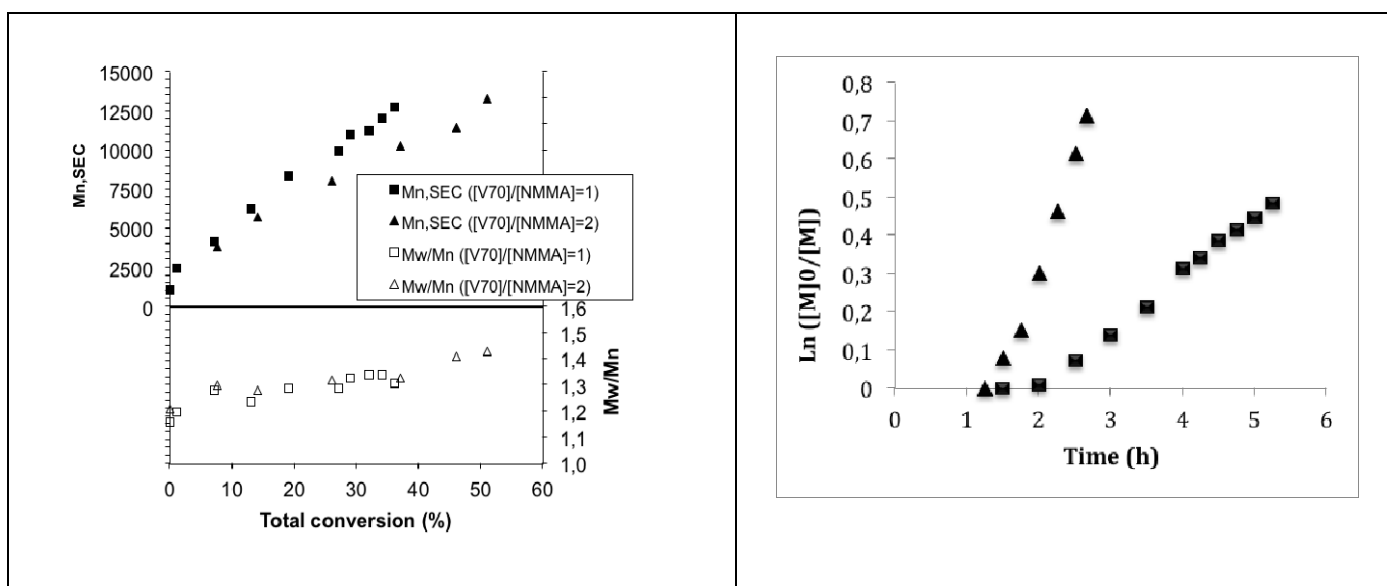


Figure S9. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the benzyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different [V70]/[NMMA] ratios. Conditions: squares: [BzMA]/[V70]/[NMMA] = 173/1/1, bulk; triangles: [BzMA]/[V70]/[NMMA] = 173/2/1, bulk.

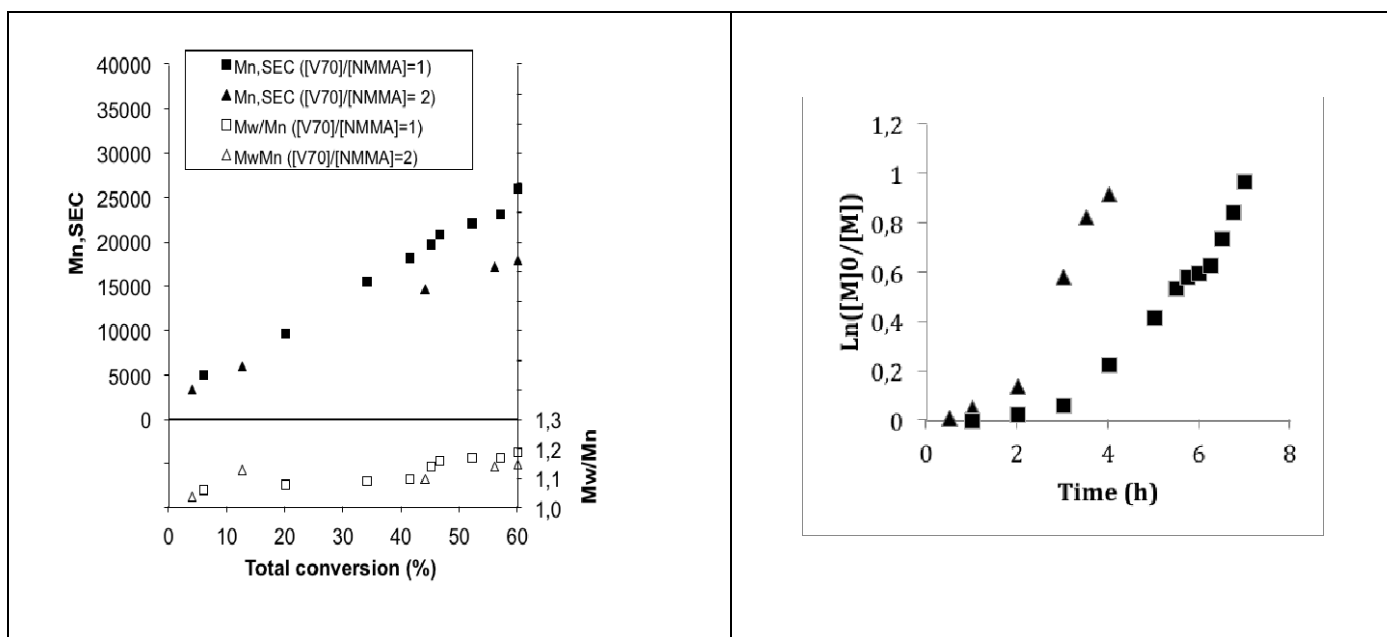


Figure S10. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the trifluoroethyl methacrylate polymerization initiated by V70 in the presence of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C using two different $[V70]/[NMMA]$ ratios. Conditions: squares: $[TFMA]/[V70]/[NMMA] = 173/1/1$, bulk; triangles: $[TFMA]/[V70]/[NMMA] = 173/2/1$, bulk.

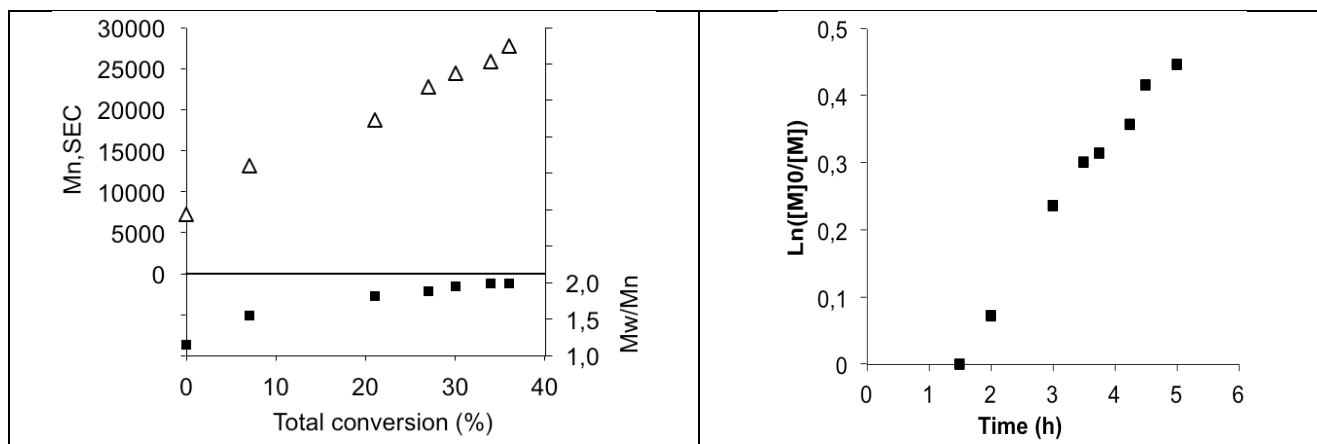


Figure S11. (a) Molar mass and polydispersity evolutions with the monomer conversion, and (b) time dependence of $\ln([M]_0/[M])$ for the methyl methacrylate polymerization initiated by V70 in the presence 9mol% styrene and of methyl-2-methyl-3-nitro-2-nitrosopropionate (NMMA) at 50°C. Conditions: $[MMA]/[St]/[V70]/[NMMA] = 247/25/1/1$, bulk.

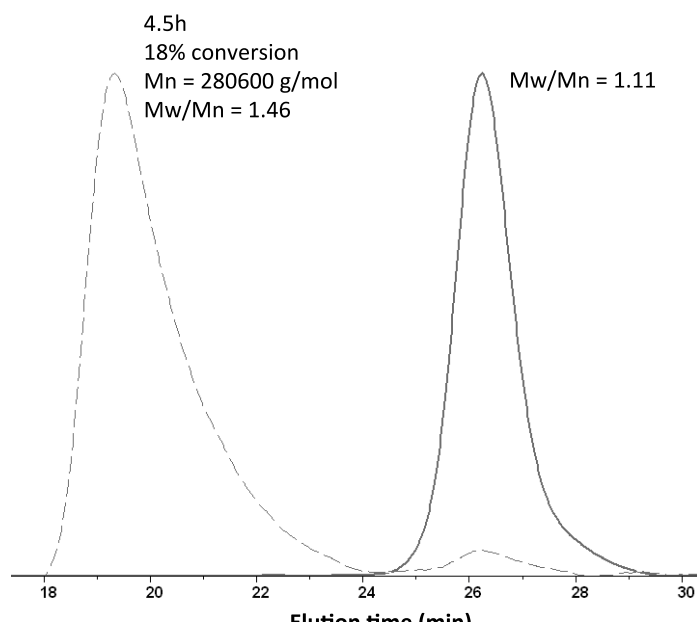


Figure S12. Resumption experiments of PMMA (Mn = 12700 g/mol; Mw/Mn = 1.11) by MMA in the bulk at 50°C. Conditions: [MMA]/[PMMA] = 11870.

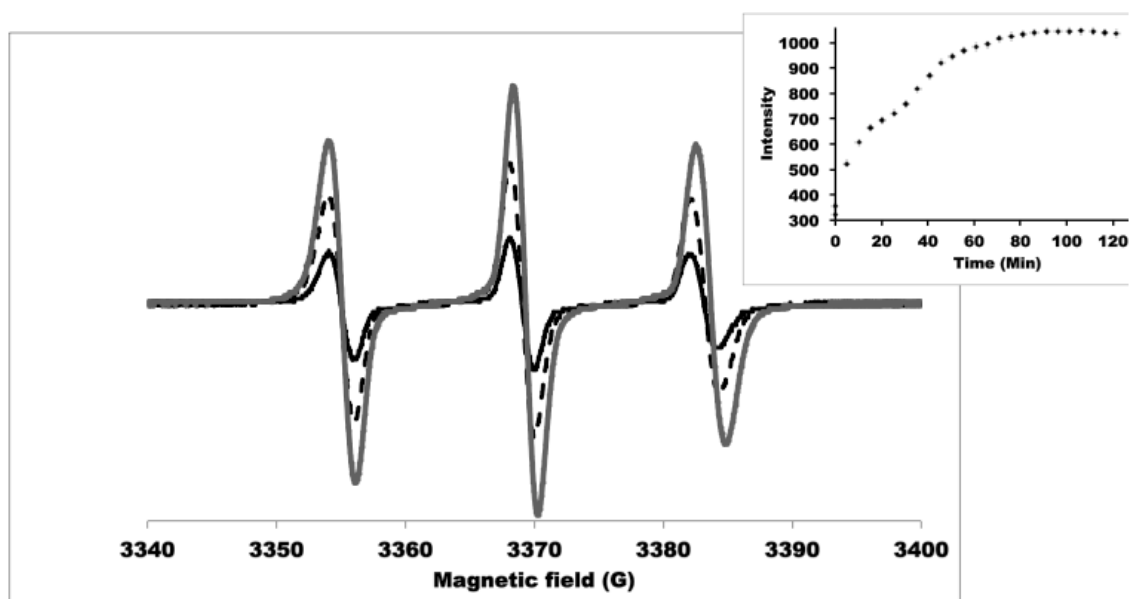


Figure S13. a) ESR spectra of the in-situ formed nitroxides formed by the reaction of V70 to NMMA after 5, 15 min and 106 min at 50°C ; b) time evolution of ESR signal intensity. Conditions: [V70]=[NMMA] = $3.4 \cdot 10^{-2}$ M in tert-butyl benzene.

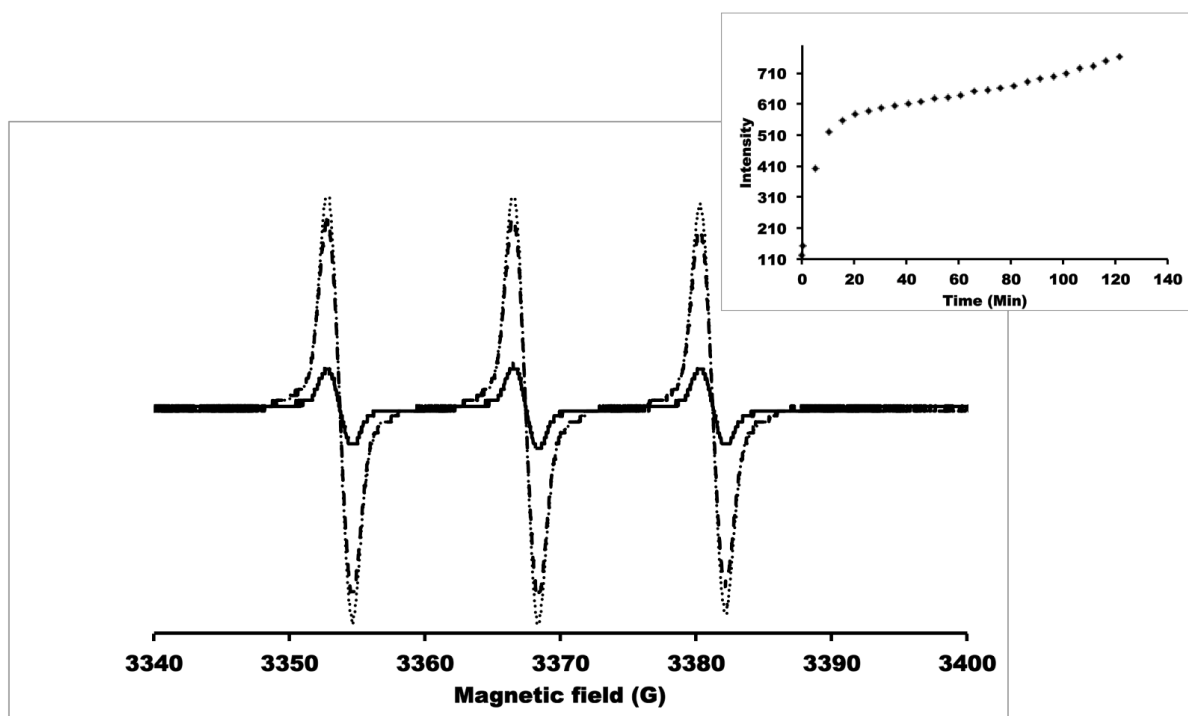


Figure S14. a) ESR spectra of the in-situ formed nitroxides by thermal decomposition of NMMA after 15 min and 55 min at 50°C ; b) time evolution of ESR signal intensity. Conditions: $[\text{NMMA}] = 3.4 \cdot 10^{-2} \text{ M}$ in tert-butyl benzene.

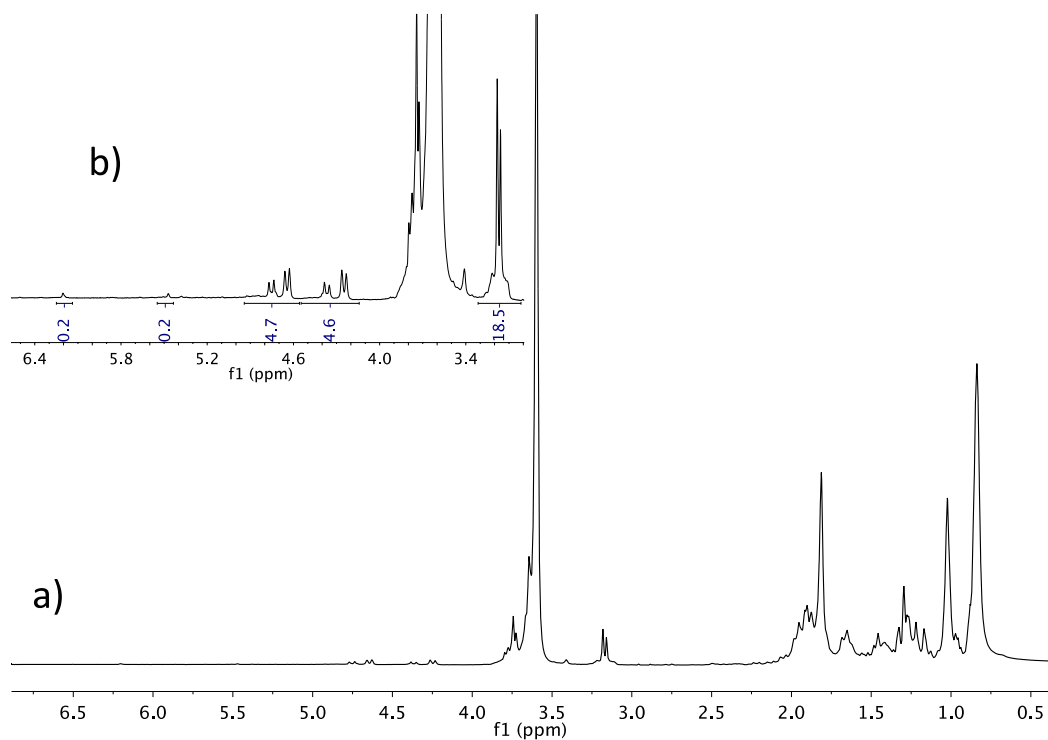


Figure S15. ^1H NMR of purified PMMA ($M_n = 2100 \text{ g/mol}$; $M_w/M_n = 1.21$) in CDCl_3 prepared by V70/NMMA at 50°C: a) full spectrum; b) 3 to 6.5 ppm enlarged region.

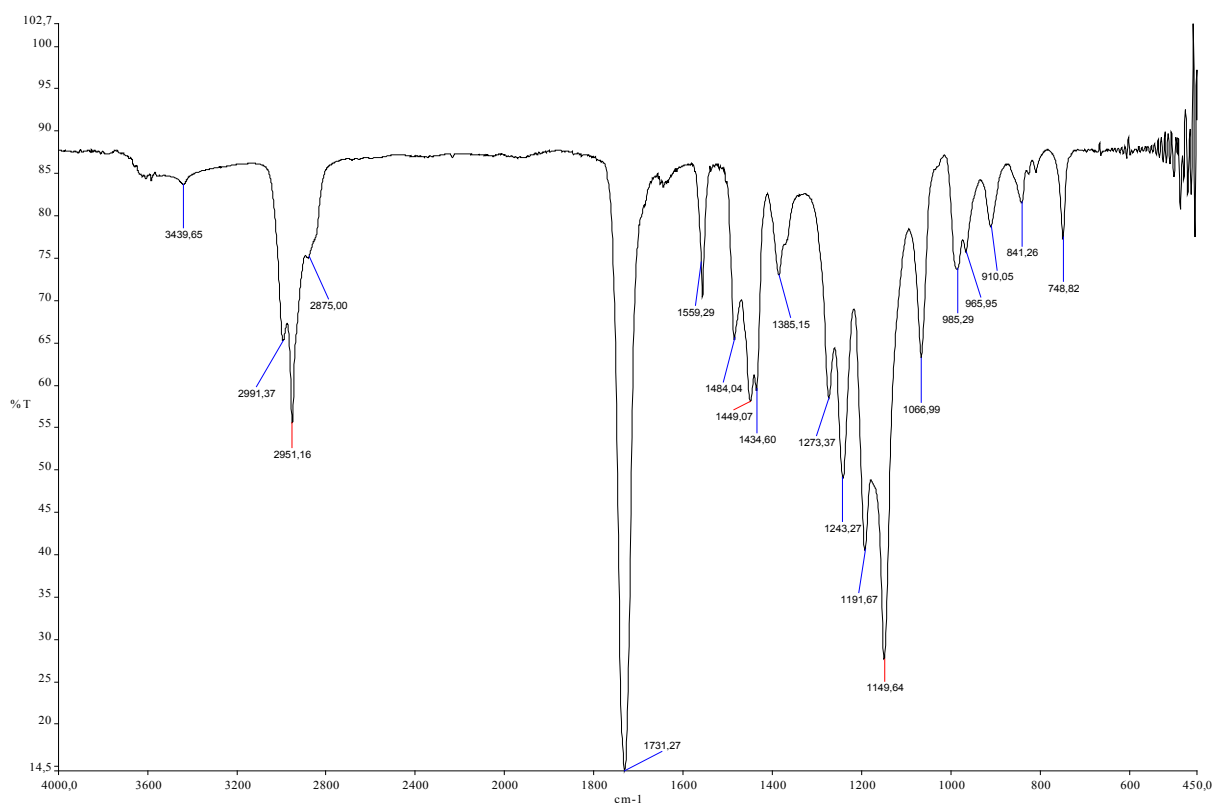


Figure S16. IR spectrum of PMMA ($M_n = 2100$ g/mol; $M_w/M_n = 1.21$) prepared by V70/NMMA at 50°C

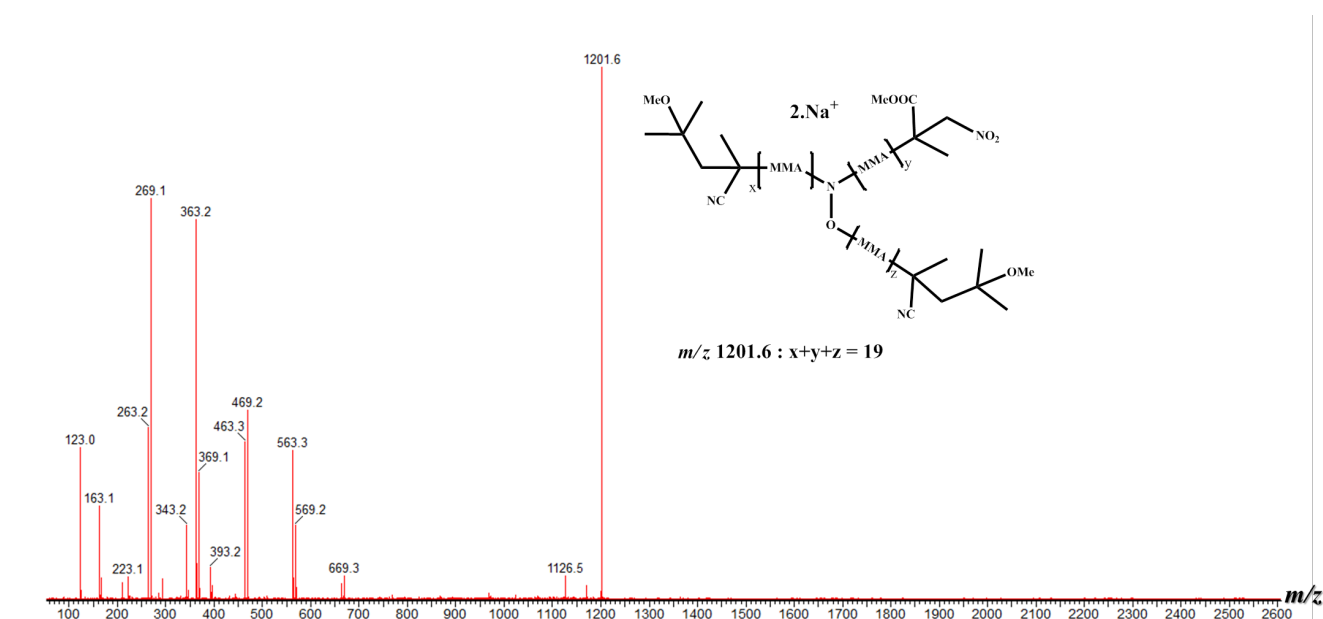


Figure S17. MSMS spectrum of m/z 1201.6 ($E_{\text{coll}} = 50$ eV; Collision gas Ar)

Without entering into details, the most important information is that, upon collisional activation, we never observed nitroxide radical ions (i.e. m/z 433, 439, 445...see Figure 6). This result confirms that the pre-cited nitroxides are probably produced in solution during the last steps of the desolvation process.

Table S1: Polymerization of HEMA and DMAEMA at 40 and 50°C using the NMMA/V70 system.

Entry	Monomer	T (°C)	Time (h)	Conv. (%)	Mn, _{SEC} (g/mol)	M _w /M _n
1	HEMA	50	1	8	4300	1.16
2	HEMA	50	2	21	15600	1.66
3	HEMA	40	6	9	7400	1.41
4	HEMA	40	13	25	17800	1.89
5	DMAEMA	50	1	16	7400	2.25
6	DMAEMA	50	2	71	22200	2.34
7	DMAEMA	40	2	13	8000	1.58
8	DMAEMA	40	5	57	24800	2.53

Conditions: [monomer]/[NMMA]/[V70]= 243/1/1 for HEMA and 174/1/1 for DMAEMA.

References

1. H. Shechter and D. E. Ley, *Chem. Ind. (London, U. K.)*, 1955, 535.
2. A. J. R. Heck and R. H. H. van den Heuvel, *Mass Spectrometry Reviews*, 2004, **23**, 368-389.