First Effective Nitroxide-Mediated Polymerization of Methyl Methacrylate

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Received October 9, 2006; Revised Manuscript Received February 12, 2007

ABSTRACT: Bulk methyl methacrylate (MMA) controlled radical polymerization was carried out using two 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO) based alkoxyamines. Whatever the alkoxyamine used, polymerization presents a controlled character, and high conversion can be reached. Polymerization up to 60% conversion, initiated with the nitro para-substituted alkoxyamine **2**, showed a linear increase of number-average molecular weight (M_n) vs conversion even at the beginning of the polymerization with the final polydispersity index (PDI) close to 1.4. A reinitiation test onto *n*-butyl acrylate has shown that even if this nitroxide is not suited for acrylate monomers, the shift of the size exclusion chromatography (SEC)-trace proved the poly(methyl methacrylate)−DPAIO macroinitiator (PMMA−DPAIO) obtained had a living character. These results showed that the range of monomers that could be polymerized by nitroxide mediated polymerization (NMP) can still be extended.

Introduction

Controlled radical polymerization (CRP) has become an easy method to prepare well-defined (co)polymers with predictable molar masses, end group functionalities and narrow molar mass distribution.[1] These properties are required to obtain tailor-made materials. Among the various techniques currently used for CRP, nitroxide-mediated polymerization (NMP) has attracted a renewal of interest because of its simplicity, since in most cases it requires only adding the suitable alkoxyamine to the polymerization system. This technique is based on the reversible dissociation of the initiating alkoxyamine and of the dormant species,[2,3] which limit irreversible terminations. Hence, the majority of dormant living chains can grow until the monomer is consumed, resulting in a polymer with large living character and a narrow molar mass distribution.

Rizzardo[4] and Georges[5] were the first to introduce the use of 2,2,6,6-tetramethyl-1-piperidynyloxyl nitroxide (TEMPO) to control the polymerization of styrene. Many nitroxides[6] have then been developed to extend this technique to different monomers. The development of acyclic nitroxides, for example *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1)[7,8] or 2,2,5-trimethyl-4-phenyl-3-azahexane nitroxide (TIPNO),[9,10] as counter radicals allowed to apply this technique to acrylate derivatives. Up to now, NMP has been criticized for its inefficiency for the control of methacrylate derivatives.[11] Thanks to its optical properties and aspect (transparency, brightness, etc.), polymethacrylate derivatives are technical polymers, used in many applications from house furnishing to optic fibers as well as in building industry and biomedical products. That is why many studies have been devoted to improving the controlled polymerization of this kind of monomers, in terms of molecular characteristics, overall architecture, nature of end groups, regio- and stereo-selectivities, and particularly block copolymer design.

Rizzardo et al.[12] tested different nitroxides belonging to the TEMPO and 1,1,3,3-tetraethylisoindolin-2-oxyl nitroxide (TEDIO) derivatives as controlling agent for the NMP of MMA. Whatever the nitroxide used, the polymerization stopped after 30−40% conversion with no living character. According to the authors,[12] these results may be explained by hydrogen atom abstraction reaction (often called disproportionation reaction) between the nitroxide and the macroradical producing hydroxylamine and double bond end-functionalized PMMA. The mechanism of this side reaction is unclear and could be also due to a non radical decay by intramolecular hydrogen transfer. The importance of this side reaction was later confirmed by Fischer,[13] who showed that the fraction of disproportionation $f_D = k_{cD}/(k_{cD} + k_{cC})$ is about 20% for PMMA macroradicals and TEMPO (Scheme 2).

In the presence of SG1, Fischer et al.[14] showed that the side reaction mentioned above did not occur. Benoit[15] performed MMA polymerization at 120 °C using a bicomponent system 2,2-azobis(isobutyronitrile) (AIBN)/SG1 and no control was observed, which can be accounted for by the too high equilibrium constant *K*. The estimated kinetic rate constants for the system MMA−SG1 highlighted that this nitroxide cannot control the MMA polymerization at 120 °C, but if the polymerization is carried out at lower temperature, partial livingness and control should be reached. However Charleux et al.[16] showed that apparent control of MMA polymerization with SG1 at high-temperature (90 °C) can be obtained by a precise procedure. Copolymerization of MMA with 4.4−8.8% of styrene showed all the characteristics of a controlled polymerization. The copolymerization approach (when a second monomer, which is well controlled by NMP, is added to the medium) used here allowed the average equilibrium constant *K* to be drastically decreased and the control obtained.

The development of tertiary SG1-based alkoxyamines,[17,18] exhibiting a very low dissociation temperature, has allowed the

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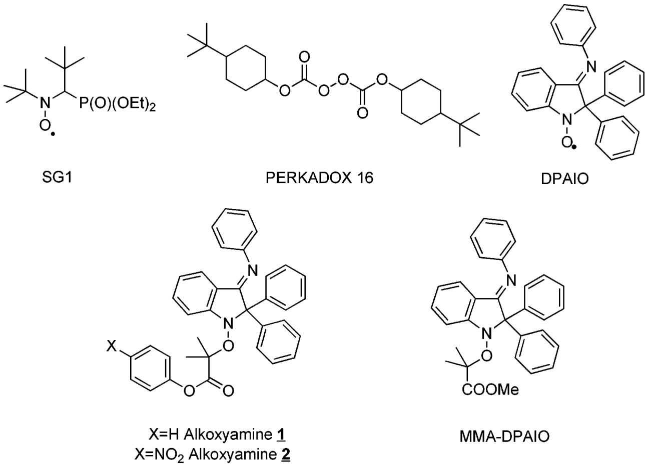
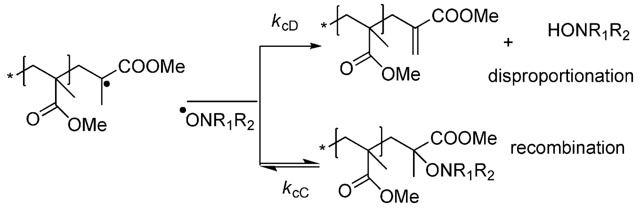
10.1021/ma062330v CCC: $37.00

Scheme 1



Scheme 2. Competition between Disproportionation and Recombination



initiation of the polymerization at a temperature below 50 °C and therefore enabled their application in MMA NMP homopolymerization.[19] Nevertheless even if a partial control occurs at the beginning of the polymerization, the couple (k_d, k_c) of the PMMA−SG1 system is not well suited for the control of the methacrylate derivatives. A penultimate effect[19] strongly accelerates the dissociation rate constant ($k_d = 10^{-2}$ s^{-1}, factor close to 35 compared to the model radical) and decreased the recombination rate constant ($k_c = 2 \times 10^4$ L mol^{-1} s^{-1}, factor close to 100 compared to the model radical), implying that the equilibrium constant $K = k_d/k_c$ became too large to allow a good control of the polymerization.

To overcome these limitations, other nitroxide than the ones usually used in NMP should be employed. This nitroxide must first not be too reactive to avoid the disproportionation side reaction. Second, according to some modelings performed using PREDICI software,[19,20] its homolysis must be slower than in the case of the SG1 analogue (by a factor close to 50) and its recombination with macroradicals faster (by a factor close to 100). Thanks to the radical delocalization on the phenyl ring which may avoid the disproportionation side reaction, we decided to focus our attention on indolynoxyl radicals. The paper presents a new alkoxyamine based on an indolynoxyl nitroxide, the 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO), which is the first nitroxide of our knowledge to be able to efficiently control the MMA polymerization (Scheme 1).

Experimental Section

Materials. Bis(*tert*-butylcyclohexyl) peroxydicarbonate (PERKADOX 16, technical grade, Fluka, >90% pure), CuBr (98%), Cu(0) (powder, 99+ %), *N,N,N′,N′,N″*- pentamethyl-diethylenetriamine (PMDETA, 99+ %), *n*-butyl acrylate (BA, 99+ %) and methyl methacrylate (MMA, 99%) were purchased from Aldrich and used as received. DPAIO was synthesized as described by Greci,[21] 2-bromo-2-methylpropionic acid phenyl ester and 2-bromo-2-methylpropionic acid 4-nitrophenyl ester were synthesized as described by Haddleton.[22]

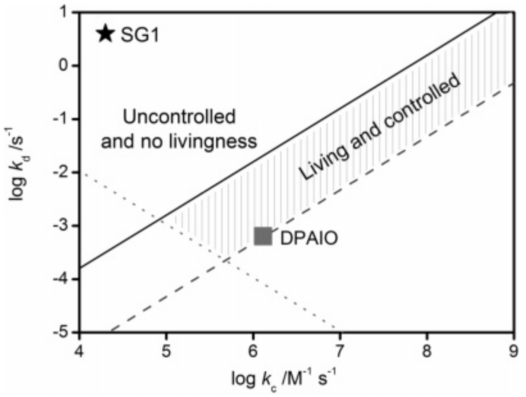


Figure 1. Predictive phase diagram at 100 °C for poly(methyl methacrylate) (PMMA). $k_p^{42} = 1.95 \times 10^3$ L•mol^{-1}•s^{-1}; $k_t = 6.05 \times 10^7$ L•mol^{-1}•s^{-1}; $[I]_0 = 2.5 \times 10^{-2}$ mol L^{-1}. Key: (dotted line) limit for control δ (=PDI-1) < 0.3; (solid line) limit for livingness Φ < 0.3 (final living fraction >70%); (dashed line) time for 90% conversion = 24 h.

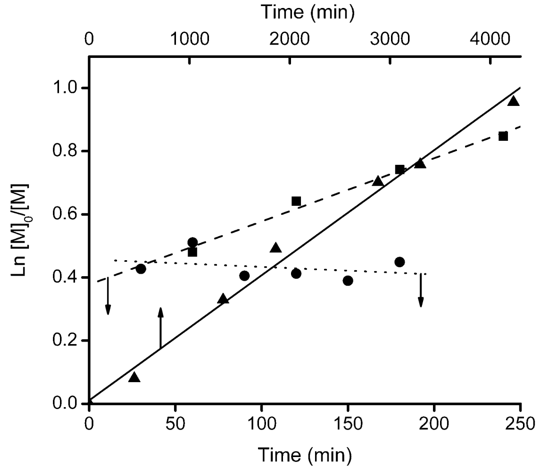


Figure 2. Experimental kinetic plot of ln ($[M]_0$/[M]) vs time for MMA bulk polymerization at 100 °C initiated with PERKADOX 16 and different amount of DPAIO nitroxide. Key: (●) no DPAIO, $[\text{Perkadox}]_0 = 3.36 \times 10^{-2}$ mol L^{-1}; (■) $[\text{DPAIO}]_0 = 2.5 \times 10^{-2}$ mol L^{-1} (targeted M_n = 40 000 g mol^{-1}) $[\text{Perkadox}]_0 = 3.25 \times 10^{-2}$ mol L^{-1}, [PERKADOX 16]/[DPAIO] = 1.3; (▲) $[\text{DPAIO}]_0 = 2.5 \times 10^{-2}$ mol L^{-1} (targeted M_n = 40 000 g mol^{-1}) $[\text{Perkadox}]_0 = 1.5 \times 10^{-2}$ mol L^{-1}, [PERKADOX 16]/[DPAIO] = 0.6; The lines correspond to the linear regression.

Analytical Techniques. ^{1}H (300.13 MHz) and ^{13}C (75.44 MHz) NMR spectra in CDCl$_3$ were recorded on a Bruker AC-300 spectrometer using 5 mm o.d. tubes. Conversion was determined by ^{1}H NMR, by comparing the intensity of the signal at 5.56 ppm and 3.6−3.75 ppm for the vinyl proton and the −OMe proton respectively. The elemental analyses were performed in a Thermo Finnigan EA 1112. The experiments were carried out under a N$_2$ atmosphere and are analyzed with the Eager 300 software. Number-average molecular weights (M_n) and polydispersity indexes (PDI) of the samples were determined by size exclusion chromatography (SEC) using a Waters 515 HPLC pump equipped with 3 Styragel columns (HR 3 (4.6 mm H 300 mm, separation between 500 and 30 000 g mol^{-1}), HR 4 (4.6 mm H 300 mm, separation between 5000 and 600 000 g mol^{-1}) and HR 5 (4.6 mm H 300 mm, separation between 2000 and 4×10^6 g mol^{-1})) and two detectors: UV/visible (Waters 486) and RI (Waters 2414). For the chromatograms shown in Figure 9, a precolumn was added to the three Styragel columns. Measurements were performed in tetrahydrofuran (THF) at room temperature, with a flow rate of 1 mL.min^{-1}. Calibration was based on Polystyrene standards (kit EasyCal Polymer Laboratories, M_n = 1180 to 377 400 g mol^{-1}) and Mark−Houwink parameters[23,24] (PS $K = 11.0 \times 10^{-5}$ dL•g^{-1}, α = 0.725; PMMA $K = 12.98 \times 10^{-5}$ dL•g^{-1}, α = 0.688). Data acquisition

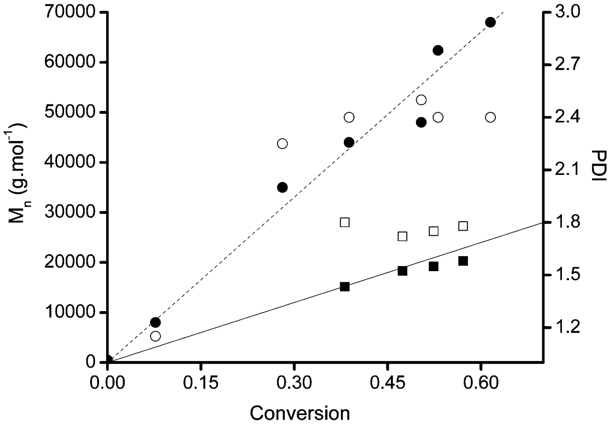


Figure 3. Evolution of M_n (full symbol) and PDI (empty symbol) vs conversion for the polymerization of MMA at 100 °C initiated with PERKADOX 16 and different amount of DPAIO nitroxide.Key: (■) $[DPAIO]_0 = 2.5 \times 10^{-2}$ mol L^{-1} (targeted M_n = 40 000 g mol^{-1}) $[Perkadox]_0 = 3.25 \times 10^{-2}$ mol L^{-1}, [PERKADOX 16]/[DPAIO] = 1.3; (●) $[DPAIO]_0 = 2.5 \times 10^{-2}$ mol L^{-1} (targeted M_n = 40 000 g mol^{-1}) $[Perkadox]_0 = 1.5 \times 10^{-2}$ mol L^{-1}, [PERKADOX 16]/[DPAIO] = 0.6. The solid line corresponds to the theoretical M_n ($M_{n,th} = (M_{MMA} \times [MMA]_0)/([DPAIO]_0) \times$ conversion) and the dashed line to the linear regression for PERKADOX 16]/[DPAIO] = 0.6.

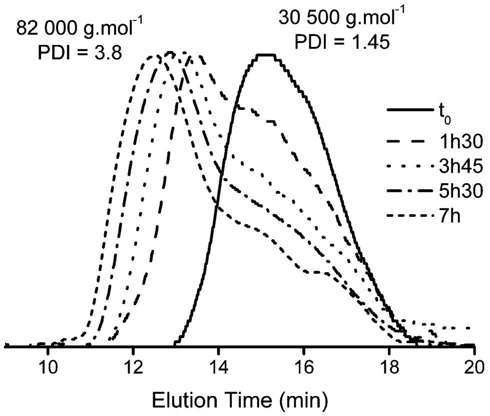


Figure 4. Raw SEC chromatograms for the reinitiation test of methyl methacrylate (7.5 g of macroinitiator in 60 mL of MMA, targeted M_n = 245 000 g mol^{-1} at 100% conversion, 100 °C) using a PMMA−DPAIO macroinitiator (bicomponent system PERKADOX 16/DPAIO = 1.3, 4 h, 57% conversion, M_n after precipitation 30 500 g mol^{-1}, PDI = 1.45).

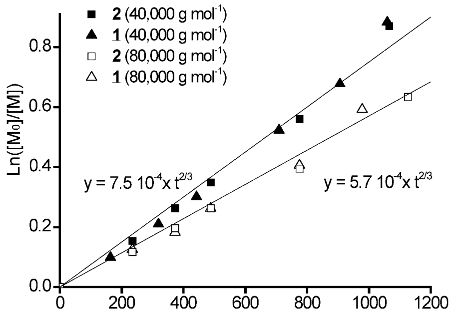


Figure 5. Kinetic plot ln $([M]_0/[M])$ vs time$^{2/3}$ for MMA bulk polymerization at 100 °C initiated with alkoxyamine **1** or **2** with two different alkoxyamine concentrations 2.5×10^{-2} mol L^{-1} (targeted M_n = 40 000 g mol^{-1}) and 1.25×10^{-2} mol L^{-1} (targeted M_n = 80 000 g mol^{-1}).

and processing were performed with Millenium 32 Waters software. Electron spin resonance (ESR) experiments were carried out on either a Bruker EMX spectrometer or a MS100 Magnetech spectrometer.

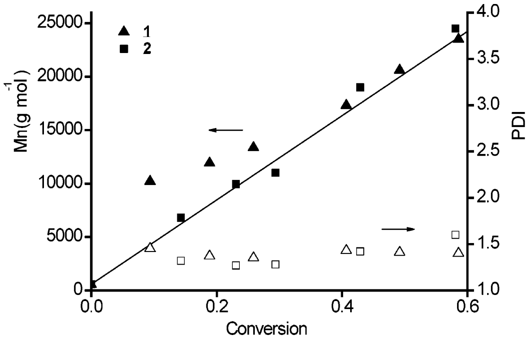


Figure 6. Evolution of number-average molar mass (M_n full symbols) and polydispersity index (PDI empty symbols) vs conversion for bulk MMA polymerization at 100 °C initiated with alkoxyamine **1** (▲) or **2** (■) with a targeted M_n = 40 000 g mol^{-1} ($[alkoxyamine]_0 = 2.5 \times 10^{-2}$ mol L^{-1}). The solid line corresponds to the theoretical M_n.

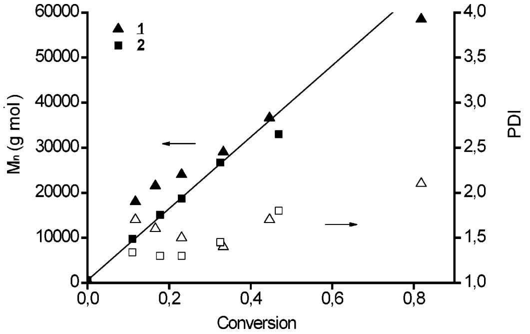


Figure 7. Evolution of number-average molar mass (M_n full symbols) and polydispersity index (PDI empty symbols) vs conversion for bulk MMA polymerization at 100 °C initiated with alkoxyamine **1** (▲) or **2** (■) with a targeted M_n = 80 000 g mol^{-1} ($[alkoxyamine]_0 = 1.25 \times 10^{-2}$ mol L^{-1}). The solid line corresponds to the theoretical M_n.

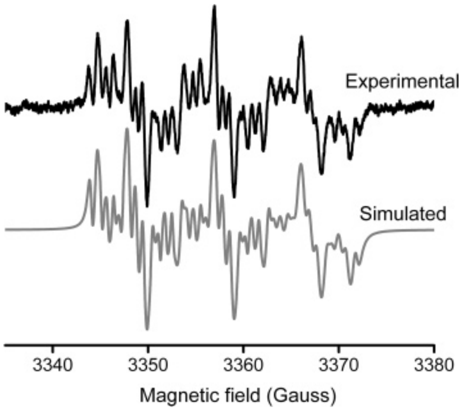


Figure 8. ESR spectra obtained after heating (2 h) a 10^{-4} M solution of PMMA−DPAIO macroinitiator in *tert*-butylbenzene. The simulated spectrum is obtained with Hfccs: a_N = 9.351 G, a_H = 3.215 G, a_H = 3.067 G, a_H = 1.055 G, a_H = 1.048 G and a_N = 0.722 G.

Phenyl 2-(2,2-Diphenyl-3-(phenylimino)indolin-1-yloxy)-2-methylpropanoate (Alkoxyamine 1). Under inert atmosphere, a solution of DPAIO (1.2 mmol, 418 mg) and 2-bromo-2-methylpropionic acid phenyl ester (1.8 mmol, 406 mg) in benzene (10 mL) was added to a deoxygenated mixture of CuBr (1.8 mmol, 240 mg), PMDETA (3.6 mmol, 579 mg), and Cu(0) (1.8 mmol, 106 mg) in benzene (10 mL). After 24 h of stirring at room temperature, the mixture was filtered through Celite, diluted with diethyl ether, and then washed with water to extract copper-based compounds. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent at room temperature under reduced pressure, the crude product was purified by silica gel column chromatography (pentane:ether = 9:1). Alkoxyamine **1** (460 mg, 0.85 mmol, yield = 71.3%) was obtained as a yellow powder. RMN

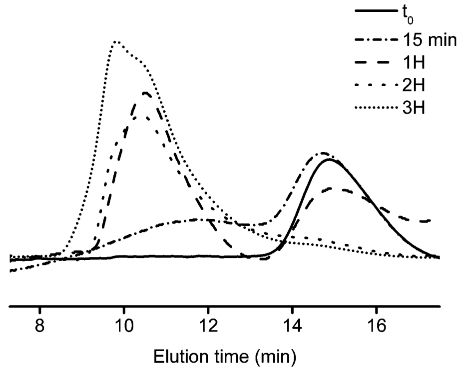


Figure 9. Raw SEC chromatograms for the reinitiation test of *n*-butyl acrylate (1 g of macroinitiator in 100 g of BA, 120 °C) using a PMMA−DPAIO macroinitiator (monocomponent system: alkoxyamine **2**, 8 h, 65% conversion, M_n after precipitation 17 000 g mol^{-1}, PDI = 1.35).

^{1}H (CDCl$_3$, 300.13 MHz): 1.30 ppm (s, 6 H); 6.31 (d, *J*(H,H) = 7,74 Hz, 1 H); 6.56 (t, *J*(H,H) = 7,56 Hz, 1 H); 6.68 (d, *J*(H,H) = 7,93 Hz, 2 H); 6.81 (d, *J*(H,H) = 8,12 Hz, 2 H); 6.99 (t, *J*(H,H) = 7,37 Hz, 1 H)); 7.12 (m, 1 H); 7.18−7.31 (m, 12 H); 7.55 (m, 4 H). RMN ^{13}C (CDCl$_3$, 75.47 MHz): 24.39 (CH$_3$); 84 and 85.33 (2s, (−CH$_3$)$_2$*C*−*C*(*O*)) and (−N−*C*(Ph)$_2$−)); 114.24; 118.05; 118.83; 121.18; 121.96; 123.53; 125.85; 126.11; 127.56; 129.28; 129.38; 130.84; 133.37; 150.61; 151.44; 158.58 (aryl carbons); 169.84 (−C=N−); 171.38 (−C=O). Anal. Calcd for $C_{36}H_{30}N_2O_3$ (538.63): C, 80.27; H, 5.61; N, 5.20. Found: C, 80.55; H, 5.81; N, 5.06.

4-Nitrophenyl 2-(2,2-Diphenyl-3-(phenylimino)indolin-1-yloxy)-2-methylpropanoate (Alkoxyamine 2). Under inert atmosphere, a solution of DPAIO (5.15 mmol, 1.93 g) and 2-bromo-2-methylpropionic acid 4-nitrophenyl ester (7.71 mmol, 2.22 g) in benzene (40 mL) was added to a deoxygenated mixture of CuBr (7.71 mmol, 1.105 g), PMDETA (15.42 mmol, 1.336 g), and Cu(0) (7.71 mmol, 490 mg) in benzene (40 mL). After 24 h of stirring at room temperature, the mixture was filtered off onto Celite, diluted with diethyl oxide, and then washed with water to extract copper-based compounds. The organic layer was dried over anhydrous MgSO$_4$. After removal of the solvent at room temperature under reduced pressure, the crude product was purified by silica gel column chromatography (pentane:ether = 4:1). Alkoxyamine **2** (1.8 g, 3.1 mmol, yield = 60%) was obtained as a yellow-orange powder. RMN ^{1}H (CDCl$_3$. 300.13 MHz): 1.46 ppm (s, 6 H); 6.41 (d, *J*(H,H) = 7.83 Hz, 1 H); 6.67 (t, *J*(H,H) = 6.57 Hz, 1 H); 6.75 (d, *J*(H,H) = 7.45 Hz, 2 H); 6.98 (d, *J*(H,H) = 9.1 Hz, 2 H); 7.08 (t, *J*(H,H) = 7.33 Hz, 1 H)); 7.29−7.82 (m, 10 H); 7.61 (m, 4 H); 8.18 (d, *J*(H,H) = 9.1 Hz, 2 H). RMN ^{13}C (CDCl$_3$, 75.47 MHz): 23.71 and 24.39 ppm (2s, CH$_3$); 83.85 and 85.28 (2s, (CH$_3$)$_2$*C*-*C*(*O*)) and (−N-*C*(Ph)$_2$-)); 113.84; 117.92; 118.64; 121.96; 122.18; 123.58; 125; 126.18; 127.64; 129.27; 130.72; 133.29; 145.20; 151.26; 155.16; 158.24 (aryl carbons); 169,51 (−C=N−); 170,38 (−C=O). Anal. Calcd for $C_{36}H_{29}N_3O_5$ (583.63): C, 74.09; H, 5.01; N, 7.20. Found: C, 73.64; H, 5.13; N, 7.12.

Typical Polymerization Experiment. A degassed (20 min nitrogen bubbling) bulk solution of methyl methacrylate (40 g, 0.4 mol) and alkoxyamine **1** (0.538 g, 1 mmol) was heated up for 10 h to 100 °C in a 100 mL Parr reactor up to 58.6 % monomer conversion. In this case a ramp of temperature (10 min) has been used. The influence of the experimental conditions have been extensively discussed in a previous work[20] and has shown that with an alkoxyamine with no low dissociation temperature (cleavage temperature T_c above 60 °C for example) the impact of the heating procedure is negligible.

The number-average molecular weight and polydispersity index (M_n = 23 500 g mol^{-1}; PDI = 1.4) of PMMA−DPAIO were determined by SEC.

Reinitiation Test. Synthesis of the Macroinitiator PMMA−DPAIO. Alkoxyamine **2** (1167 g, 2 mmol) was added to a solution of methyl methacrylate monomer (40 g, 0.4 mol) and then degassed by 15 min of nitrogen bubbling in a 100 mL Parr reactor. The polymerization was carried out for 8 h at 100 °C. The mixture was cooled in an ice−water bath to stop the reaction and then the polymer was precipitated in ethanol. Conversion (65%) was determined by ^{1}H NMR spectroscopy. The number-average molecular weight and polydispersity index (M_n = 17 000 g mol^{-1}; PDI = 1.35) of PMMA−DPAIO were determined by SEC.

Table 1. Determination of k_c for the PMMA−DPAIO System[a]

method	Mayo (M_n)	CLD
kinetic chain length	M_n = 33 300 g mol^{-1}	d[ln(x_i)]/di = 3.1 × 10^{-3}
k_c (L·mol^{-1}·s^{-1})	1.4 × 10^6	1.45 × 10^6

[a] T = 40 °C, [DPAIO]$_0$ = 1 × 10^{-5} mol L^{-1}, [DMPA]$_0$ = 10^{-2} mol L^{-1}, and [M]$_0$ = 9.36 mol L^{-1}.

Synthesis of PMMA-*b*-PBA. *n*-Butyl acrylate monomer (100 g, 0.781 mol)) was added to 1 g (5.8 × 10^{-5} mol) of the PMMA−DPAIO macroalkoxyamine and degassed by 30 min of N$_2$ bubbling. The round-bottom flask was sunk in a pre-heated oil bath at 120 °C. The polymerization was carried out for 3 h with a magnetic stirring. Sampling was performed and the raw mixture was analyzed by SEC.

Results and Discussion

To improve the controlled and the living character of the bulk NMP MMA polymerization, two distinct criteria should be fulfilled. The first one is related to the ability of the PMMA macroradical to undergo the H-transfer reaction or disproportionation reaction between the macroradical and the nitroxide. This side reaction avoided any attempts to obtain a successful controlled polymerization. If this criterion is fulfilled, the second one is related to the more classical problem: the value of the equilibrium constant *K*.

We showed previously[19] that the PMMA SG1-based macroalkoxyamine and PMMA macroradical have a different behavior vs the dissociation and recombination reaction than the poly(butyl acrylate) (PBA) or polystyrene (PS) ones. The bulkiness of the penultimate tertiary unit implied a strong acceleration of the homolysis rate constant and a strong decrease of the recombination rate constant leading to a too important value of the equilibrium constant *K* to control the polymerization. This effect should be taken into account for the choice of the desired nitroxide.

Because of the radical delocalization[25] on the phenyl ring, which may decrease the spin density on the oxygen atom and therefore decrease the ability to undergo disproportionation, we decided to study the indolynoxyl radical family and the corresponding alkoxyamines. The 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide or DPAIO synthesized by Greci et al.[21] is thermally stable up to 200 °C[26] and had already shown an interest for the control of the radical polymerization of ethylene.[27] A first study of the reactivity of this nitroxide toward PMMA macroradicals has been carried out in our lab:[28] an ^{1}H NMR analysis of the polymer (ethylenic protons at 5.5 and 6.2 ppm) obtained after a conventional polymerization and a polymerization in presence of DPAIO (bulk, 125 °C, initiated by MMA−DPAIO) presented respectively 45 and less than 15% of functionality showing that DPAIO mainly did not disproportionate with PMMA macroradicals.

The kinetic constants for the system PMMA−DPAIO has then been determined. The recombination rate constant k_c between PMMA macroradicals and DPAIO was measured at 40 °C using the radical nitroxide recombination−pulsed laser polymerization−size exclusion chromatography (RNR−PLP−SEC) method[29] and gives a k_c value close to 1.4 × 10^6 L mol^{-1} s^{-1} (Table 1). Nitroxides are paramagnetic species that can easily be observed by means of electron paramagnetic resonance (EPR)

Table 2. Experimental Conditions and Results of the Bulk Polymerizations of Methyl Methacrylate at 100 °C

entry	initiator	nitroxide[a]	targeted M_n (g mol^{-1})	time (h)	convn (%)	M_n/M_{nth} (g mol^{-1})	PDI
1	PERKADOX 16	DPAIO ($r = 1.3$)	40 000	4	57	20 300/22 900	1.75
2	PERKADOX 16			3	33		
3	PERKADOX 16	DPAIO ($r = 0.6$)	40 000	70.5	62	68 000/25 000	2.4
4	**1**		40 000	10	59	23 500/23 500	1.4
5	**1**		80 000	25	82	58 800/65 500	2.05
6	**2**		40 000	9.5	58	24 500/23 300	1.55
7	**2**		80 000	10.5	47	33 000/37 500	1.75
8	**2**		20 000	8	65	17 000/12 400	1.35

[a] $r = [\text{PERKADOX 16}]_0/[\text{DPAIO}]_0$

spectroscopy, and thus this technique is mainly used to measure the dissociation rate constant k_d. Nevertheless the spectra of the DPAIO nitroxide is very complex due to some hyperfine couplings deriving from the nitrogen in position 3 and from the protons of the condensed aromatic ring and of the substituent in position 2 and is also very dependent on the oxygen concentration which is known to broaden the width of the spectra. It was therefore difficult to carry out precisely the measurement of the k_d value (alkyl scavenger: oxygen) when the spectra depends on the conditions. However, Le Mercier et al.[30] showed that the cleavage temperature T_c can be easily related to the k_d value using structure−reactivity relationships.[31] The cleavage temperature T_c of the model alkoxyamine MMA−DPAIO (Scheme 1) was measured to be 90 °C and so using eq 1, its k_d value at 120 °C was predicted to be around 1.95×10^{-4} s^{-1}.

$$\log k_d/s^{-1} = 1.51(\pm 0.26) - 0.058(\pm 0.003) \times T_c/°C \tag{1}$$

The effect of the bulky PMMA chain must be taken into account to determine the k_d value for the macromolecular species. This effect (a 30-fold increase of k_d) could be estimated with structure−reactivity relationships;[32] that is, the activation energy E_a for the PMMA−DPAIO should be close to 125.6 kJ mol^{-1}.

To determine the reaction temperature for the polymerization, we used the Fischer's diagram[33] linking the couple of kinetic rate constants (k_d, k_c) of the system PMMA−DPAIO at a given temperature with the controlled (δ, the residual polydispersity at the end of the reaction) and living character (Φ, the fraction of dead chains at the end of the reactions). The equations developed by Fischer formed in the (k_d,k_c) space, different areas permitting to predict whether or not the polymerization is controlled and/or living (Figure 1). As k_c is only weakly dependent on the temperature, we can determine the optimized k_d value for having a living and controlled polymerization. The knowledge of the activation energy thus allowed us to determine the optimized temperature.

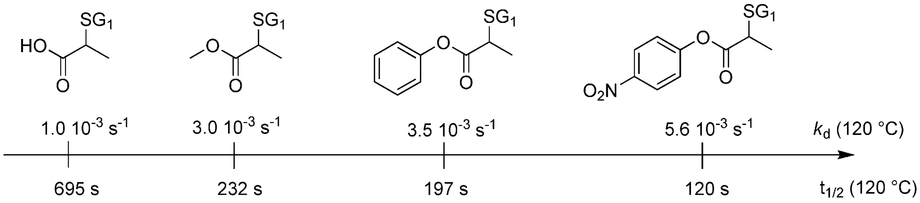
At 100 °C, the couple of kinetic constants seems allowing a living and controlled polymerization (Figure 1) with high conversion in an acceptable polymerization time (below 24 h). In a preliminary study the polymerization has been carried out in a bicomponent system. We have chosen the bis(*tert*-butylcyclohexyl) peroxydicarbonate PERKADOX 16 as initiator to reach a fast initiation at 100 °C (half-life time of 40 s at 100 °C). The experimental conditions are summarized in Table 2.

With this initiator, if there was an increase of conversion during the polymerization time, this should be induced by a reversible equilibrium between dormant and active species. A blank experiment realized without any nitroxide (Table 2, entry 2, and Figure 2) presented a constant conversion during all the polymerization time showing that no active species was present after the rapid initiation. Because of the high dissociation rate of the initiator the first experiment is carried out with an excess of initiator to prevent the loss of active radicals by primary radical termination. The ratio [initiator]/[nitroxide] was 1.3. The evolution of the ln $[M]_0/[M]$ vs t plot is presented on the Figure 2 and showed a linear increase characteristic of a polymerization with a constant macroradical concentration. The origin of the linear correlation did not go through 0 because the excess of initiating radical created at the beginning of the polymerization a first population (representing 30% of conversion in less than 10 min) of dead chains. Once the equilibrium was set up, the controlled polymerization can be obtained. The evolution of the molecular weight M_n vs conversion showed also an increase but the excess of initiating radical did not allow to obtained low PDI (see Figure 3). A second attempt was carried out with a ratio of 0.6 to have an equal amount of initiating radicals and nitroxide. The evolution of the ln $[M]_0/[M]$ vs t was always linear but with an initial origin close to zero. The rate of these two polymerizations was different due to the difference of the initiation which caused a different concentration of free nitroxide in the medium. The evolution of M_n vs conversion presented a low efficiency (close to 30%) which could be due to a too low value of the [initiator]/[nitroxide] ratio (inhibition of the polymerization) or which can be due to a problem during the initiation (consumption of primary alkyl radicals). Indeed the probability of the first adduct of the initiating radical R−M$^\bullet$ to recombine with nitroxide is higher than the radical to propagate ($k_c[\text{DPAIO}]_0 > k_p[\text{M}]_0$). The k_d value of the R−M−DPAIO compound should be lower than the one of the polymeric PMMA−DPAIO due to the lack of the penultimate effect in the case of the adduct. A lot of active species could be blocked with a DP = 1 and when another monomer was inserted, the penultimate effect increased the rate of polymerization. This could be related to the increase of the polydispersity index during the reaction time.

In order to check the living character of the previous PMMA−DPAIO, a first reinitiation test with methyl methacrylate as second monomer was performed with the PMMA−DPAIO obtained with the ratio [initiator]/[nitroxide] of 1.3. Even if the precursor was polluted by a nonnegligible population of dead chains, the clear shift of the raw SEC trace (Figure 4) indicated that the polymerization of MMA mediated by the DPAIO nitroxide is controlled and living. Encouraged by these preliminary results, we have been investigating the initiation of the polymerization by a monocomponent system in order to improve the controlled and living character of the polymerization, as already reported by Hawker.[34]

Using different SG1-based alkoxyamines, we have shown[20] that the value of the initiating dissociation rate constant k_{d1} plays a pivotal role for the success of NMP process. If the initiating alkoxyamine decomposes too slowly with respect to the macroalkoxyamine or to the polymerization time, no linear evolution of the M_n vs conversion can be obtained. The penultimate effect which occurred during the MMA nitroxide-mediated polymerization implied to use an initial alkoxyamine

Scheme 3. Comparison of the Dissociation Rate Constant k_{d1} and of the Half-Time $t_{1/2}$ at 120 °C for Different SG1-Based Alkoxyamines (Isomer RS/SR)



with a very high dissociation rate constant and at least even higher than the MMA−SG1 model alkoxyamine. The choice of the alkyl moiety is thus crucial for the success of the polymerization. By analogy with SG1 analogues alkoxyamines,[35,36] the acceleration of the dissociation rate constant can be achieved using a released alkyl moiety with long range polar effect (see Scheme 3).

Alkoxyamines **1** and **2** based on phenyl methacrylate moiety were chosen to have a fast initiation. These alkoxyamines were prepared according to the atom transfer radical addition (ATRA) method[37] in 75 and 60% yield, respectively.

Polymerizations using two different concentrations of the two alkoxyamines (respectively targeted M_n of 40 000 and 80 000 g mol^{-1}) have been carried out at 100 °C. On Figure 5, the kinetic plots ln $[M]_0/[M]$ vs $t^{2/3}$ are linear for both alkoxyamines and the slopes depend on the initial alkoxyamine concentration. This result has already been stated by Fischer[2] when he highlighted the establishment of the persistent radical effect PRE during the polymerization process (eq 2).

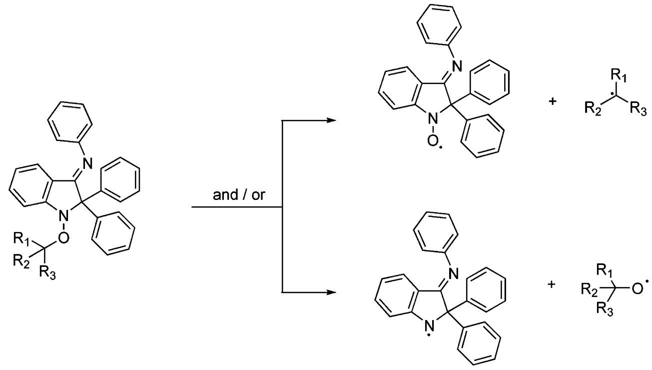
$$\ln \frac{[M]_0}{[M]} = \frac{3k_p}{2}\left(\frac{k_d[\text{alkoxyamine}]_0}{3k_t k_c}\right)^{1/3} t^{2/3} \qquad (2)$$

Lutz et al.[38] have experimentally observed these unusual kinetic laws and have determined the pseudo equilibrium constant for the SG1−styrene system. The slope ratio for the two concentrations is equal to 1.31, which is close to the theoretical value ($2^{1/3} = 1.26$) determined with eq 2.

As shown in Figures 6 and 7, when alkoxyamine **1** was used as initiator for the MMA polymerization at 100 °C, the evolution of the molar masses vs conversion both showed a regular increase of the M_n characteristic of a controlled polymerization. Nevertheless at the beginning of the polymerization (conversion <30%), the experimental M_n were slightly higher than the theoretical ones, which was due to a relatively slow initiation. The slow decomposition of the starting alkoxyamine caused relatively high PDI (close to 1.4 for a targeted M_n of 40 000 g mol^{-1} at 60% conversion). For high targeted M_n and/or high conversion (up to 60% conversion) the PDI increased because the polymerization mixture has become very viscous and this phenomenon leaded to a decrease of the rate of recombination with the nitroxide and the loss of the control. This could be monitored in the ln $[M]_0/[M]$ vs $t^{2/3}$ plot (see Supporting Information) where the linearity is lost for conversion up to 60%.

In order to increase the dissociation rate constant of the initiating alkoxyamine, we used alkoxyamine **2** to polymerize the MMA. On the basis of our studies with SG1-derivatives alkoxyamines, the presence of nitro group in para position of the phenyl ring should accelerate the k_{d1},[35] due to a long-range polar effect. Actually the substitution of alkoxyamine **1** by the nitro-based alkoxyamine **2** (Figure 6 and 7) allowed the control of the polymerization (experimental M_n close to theoretical ones and low PDI) even at the beginning of the polymerization (before 30% of conversion).

Scheme 4. The Two Modes of Decomposition for a 2,2-Diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl Nitroxide (DPAIO) Based Alkoxyamine



With the nitro-based alkoxyamine, the polymerization is well controlled up to 60 or 70% of conversion, but to be fully complete we have also checked the livingness of the prepared polymer. In a first step we have performed a bulk MMA polymerization with a targeted M_n of 20 000 g mol^{-1} (Table 2, entry 8). The polymerization reaction was quenched at 65% of conversion (8 h) and the polymer was purified by precipitation in ethanol. The prepared PMMA−DPAIO macroinitiator had a M_n of 17 000 g mol^{-1} with a PDI = 1.35. When the polymer was heated in *tert*-butyl benzene for 2 h, the ESR spectra of the DPAIO was observed (see Figure 8) assessing the presence of living chains.

In a second step the macroinitiator was used to prepare a diblock copolymer PMMA-*b*-PBA by initiation of *n*-butyl acrylate (BA). To have a significant shift of the SEC trace, the concentration of the macroinitiator was very low: 1 g of PMMA−DPAIO for 100 g of *n*-butyl acrylate, i.e., 13280 equiv). The result of the reinitiation test is displayed in Figure 9. The quasi-complete disappearance of the macroinitiator peak (retention time 15 min) proved that the PMMA−DPAIO was highly living. The difference between the d*n*/dc values for the two blocks (0.06 for PBA[39] and 0.09 for PMMA[40]) allowed a comparison between the homo and block polymer even if the concentration of the two species were not similar. The shift of the raw SEC trace was nevertheless not continuous (Figure 9) and the second polymerization was not controlled. This was explained by the lack of penultimate effect when some *n*-butyl acrylate unit were inserted, compared to the methyl methacrylate unit. Moreover, the k_d and k_c value for the system PBA-DPAIO are not well suited to have a controlled and living polymerization. The too low k_d value (combined with the too high k_c value) has inhibited the polymerization and therefore only a very few cycle activation/deactivation occurred in the system.

For high reaction time, a bimodal distribution appeared. This second population could be due to a competitive way of decomposition which occurred with the DPAIO-based alkoxyamines. We have shown[41] that when the alkyl moiety of the DPAIO-based alkoxyamines was a stabilized secondary radical (as the terminal *n*-butyl acrylate radical), the N−O bond dissociation occurred (50% of N−O bond dissociation) leading to an alkoxyl radical (Scheme 4). This radical could propagate until an irreversible termination occurred. The mix between these chains and the one bearing the DPAIO end group may induce this bimodal MWD.

Conclusions

Nitroxide-mediated bulk polymerization of methyl methacrylate was successfully carried out in the presence of a new alkoxyamine based on DPAIO nitroxide. High conversion (up to 80%) can be reached, which indicated that no disproportionation occurred even though the mixture was very viscous. With the nitro para-substituted alkoxyamine **2** and for conversion up to 60%, controlled PMMA with final PDI close to 1.3−1.4 can be obtained at 100 °C. The livingness of the previously prepared PMMA−DPAIO was evidenced by a reinitiation test in presence of *n*-butyl acrylate at 120 °C. However the controlled polymerization of both monosubstituted vinylic monomers (*n*-butyl acrylate or styrene as example) and disubstituted vinylic monomers such as methacrylate derivatives seemed difficult due to incompatible (k_d, k_c) values because of penultimate effect. Nevertheless, with the combination of modeling, the determination of kinetic constants and the complete understanding of the reactivity of nitroxides and alkoxyamines, the extent of the range of NMP polymerizable monomers is still possible.

Acknowledgment. ARKEMA, the University of Provence, and the CNRS are thanked for their financial support.

Supporting Information Available: Figure showing the detail of the kinetic plot (Figure 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA062330V