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COMMUNICATION TO THE EDITOR

Joining Efforts of Nitroxide-Mediated Polymerization (NMP) and Cobalt-Mediated Radical Polymerization (CMRP) for the Preparation of Novel ABC Triblock Copolymers

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Nitroxide-mediated polymerization (NMP) is a very attractive controlled radical polymerization technique that allows the preparation of very well-defined polymers by using a combination of a nitroxide (in situ formed or not) and a free-radical initiator[1−4] or by employing alkoxyamines as both initiators and controlling agents.[5−7] This powerful technique is especially attractive because it is metal-free and the polymers formed are not colored and can be directly used after synthesis without any purification step. Moreover, the development of highly efficient and commercially available alkoxyamines such as BlocBuilder has now allowed the preparation of a large range of block copolymers[8−11] even at the industrial scale (for instance, poly(methyl methacrylate)-*b*-poly(butyl acrylate)-*b*-poly(methyl methacrylate) commercialized under the name of Nanostrength from Arkema) that are mainly sold as polymer compatibilizers or additives for reinforcement of polymer matrices.

The main limitation of NMP is the range of monomers that can be effectively controlled. Some efficient alkoxyamines and nitroxides are able to control most of the conjugated vinyl monomers such as styrene and derivatives, acrylates (including some functional acrylates),[6,7,12−14] acrylamides,[6,7] acrylonitrile,[6,7] and methacrylates (with some limitations)[3,4,15−19] but also some dienes such as isoprene.[2,20,21] However, very reactive monomers such as vinyl acetate cannot be controlled by NMP because the C−ON bond at the polymer chain-end of the dormant chain cannot be cleaved at a reasonable temperature. Once the poly(vinyl acetate) chains are trapped by the nitroxide, the chains cannot be reactivated further to allow chain extension.[22]

Recently, cobalt(II) acetylacetonate ($Co(acac)_2$) in combination with V70 (2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) as initiator was demonstrated to be highly active for controlling the radical polymerization of nonconjugated nucleophilic monomers such as vinyl acetate (VAc)[23−25] and *N*-vinylpyrrolidone (NVP).[26,27] This process called "cobalt-mediated radical polymerization (CMRP)" was an extension of the pioneering work of Wayland et al. that used cobalt(II) porphyrins for controlling the acrylates polymerizations.[28] Although $Co(acac)_2$ was very active for nucleophilic monomers, no control of the polymerization was observed for conjugated monomers such as styrene and (meth)acrylates because the C−Co bond at the polymer chain end was too labile. An exception was acrylonitrile which was efficiently controlled provided that the polymerization was carried out in some polar solvents such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) at a low temperature (0 °C).[29] More importantly, the block copolymerization of vinyl acetate with acrylonitrile was also possible in these solvents starting from poly(vinyl acetate) (PVAc) as the first block.[29,30] For this block copolymerization, the acrylonitrile polymerization occurred according to a reversible termination (RT) mechanism, where the metal complex ($Co(acac)_2$) is the controlling agent and traps reversibly the polymer chains, in the same way as nitroxides in a NMP process.

Moreover, it was demonstrated that addition of a nitroxide such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) to PVAc−$Co(acac)_2$ preformed by CMRP lead to an irreversible cobalt/nitroxide exchange reaction, with release of the cobalt complex.[31] The latter was easily removed by filtration onto silica, and low cobalt-containing polymers end-capped by TEMPO were recovered. Noteworthy, TEMPO-like nitroxides bearing functional groups were also used for the chain-end functionalization of polymers preformed by CMRP.[31,32] Although it was very tempting to reinitiate the polymerization of a vinyl monomer by NMP from the PVAc−TEMPO chain-end, the C−ON bond of the alkoxyamine was stable at least until 180 °C, which makes the synthesis of well-defined diblock copolymers by NMP not possible.[32]

In this Communication, CMRP is combined for the first time with NMP, giving access to novel ABC triblock copolymers based on a nonconjugated monomer (vinyl acetate) and conjugated ones (such as acrylonitrile, styrene, *n*-butyl acrylate, or 4-vinylpyridine). Contrary to the above-mentioned studies, novel copolymers prepared by CMRP and postfunctionalized with SG1 (*N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl; see Scheme 1) nitroxide leads to a C−ON bond sufficiently labile to promote chain extension by NMP, provided that the alkoxyamine is in an activated position (at the α-position of a nitrile group for instance). SG1 was used because, due to both polar and steric effects, the corresponding SG1-based alkoxyamines exhibit faster dissociation rate constant[33] than TEMPO-based alkoxyamines. Moreover, SG1 is one of the most potent nitroxides reported so far, allowing the control of a wide range of monomers including styrenics,[34] acrylates,[34] dimethylacrylamide,[35,36] or acrylic acid.[37]

Our new strategy for the synthesis of novel ABC triblock copolymers consists of three main steps represented in Scheme 1: (i) synthesis of a PVAc-*b*-PAN diblock copolymer end-capped by $Co(acac)_2$ via sequential CMRP of VAc and AN; (ii) cobalt/SG1 exchange reaction in order to functionalize the diblock chain-end with SG1; (iii) initiation of the polymerization of a third vinyl monomer by NMP by homolytic cleavage of the C−ON bond at the diblock copolymer chain-end.

The first block, PVAc−$Co(acac)_2$, was prepared by CMRP using $Co(acac)_2$ as the controlling agent and V70 as the initiator at 30 °C in the bulk.[24] The diblock copolymer $PVAc_{237}$-*b*-PAN_{90}-$Co(acac)_2$ was then synthesized by adding acrylonitrile to the PVAc−$Co(acac)_2$ in solution in DMF at 0 °C, as reported elsewhere.[30] At 0 °C in DMF, the C−Co bond at the polymer chain-end is labile, and the polymerization of acrylonitrile occurs according to a reversible termination mechanism. When the desired molecular weight was reached for the second block (PAN), a degassed solution of excess nitroxide (SG1; ∼4 equiv compared to polymer chains) was rapidly added to end-cap the growing polymer chains by SG1, while $Co(acac)_2$ was released. At room temperature, the C−ON bond at the PVAc-*b*-PAN-SG1

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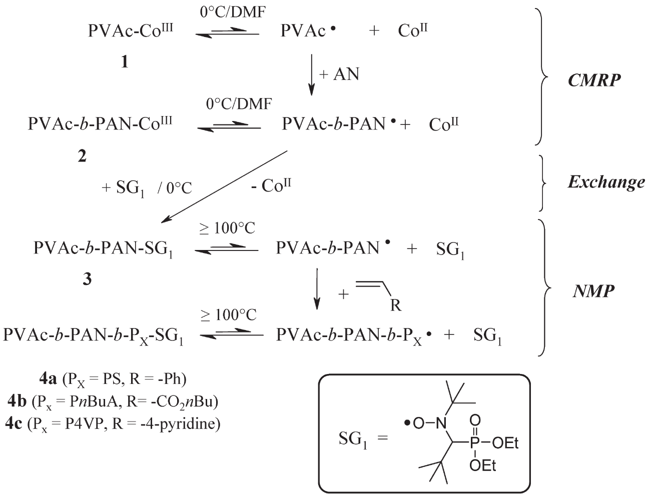
Scheme 1. General Strategy for Producing the ABC Triblock Copolymers by Combining Cobalt-Mediated Radical Polymerization (CMRP) and Nitroxide-Mediated Polymerization (NMP); Structure of SG1 Nitroxide (*N*-(2-Methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl), DMF = Dimethylformamide



chain-end is stable such that the acrylonitrile polymerization was stopped when adding SG1 (see Supporting Information Figure S1). Several precipitations in methanol/water (80/20) allowed to remove 87% of the cobalt from the copolymer (cobalt content: $[\mathrm{Co}]_{\mathrm{final}}$ = 315 ppm by ICP, $[\mathrm{Co}]_0$ = 2300 ppm, where $[\mathrm{Co}]_0$ = cobalt content before addition of SG1 and $[\mathrm{Co}]_{\mathrm{final}}$ = cobalt content after addition of SG1 and polymer purification). These precipitations are also necessary to remove the excess of SG1 that would prevent chain extension to occur. Indeed, this excess would completely shift the dormant/active species equilibrium toward the dormant one, avoiding any polymerization.

The presence of the SG1 at the chain-end and the yield of functionnalization were determined by electron spin resonance (ESR). Typically a DMF solution (10^{-4} M) of the previously prepared PVAc-*b*-PAN copolymer end-functionalized by SG1 was heated (100 °C) under argon, in presence of 5 equiv of TEMPO (to suppress the recombination reaction) for 2 h. The characteristic ESR spectrum of SG1 was observed assessing the presence of SG1 living chains. By comparing the area of the ESR SG1 spectrum released by the polymer with the one obtained with a free sample of SG1 in DMF solution (10^{-4} M) chosen as reference, the yield of functionnalization was estimated around 90 ± 5%.

The resulting PVAc-*b*-PAN copolymer end-functionnalized by SG1 was then used as macroinitiator for the NMP of styrene (Sty), *n*-butyl acrylate (*n*-BuA), and 4-vinylpyridine (4VP). Results of these copolymerization experiments are shown in Table 1.

Chain extension of PVAc-*b*-PAN-SG1 by styrene was first considered. The PAN sequence being not soluble in styrene, the polymerization was carried out in DMF at 120 °C. After 5.5 h about 75% conversion was obtained, and the SEC chromatogram of the starting diblock copolymer was clearly shifted toward the shorter elution times, in total agreement with the successful resumption of the polymer chains and the formation of the PVAc-*b*-PAN-*b*-PS triblock copolymer (Figure 1). The polydispersity of the copolymer remained quite low (M_w/M_n = 1.31).

^{1}H NMR analysis of the copolymer evidenced the presence of signals typical of PVAc, PAN, and PS blocks (Figure 2). The composition of the copolymer and the molecular weight of the sequences were determined by ^{1}H NMR by comparison of the intensities of the signals corresponding to $\mathrm{CH_2{-}C}H\mathrm{{-}OCOCH_3}$ of PVAc (at 4.82 ppm), to $\mathrm{CH_2{-}C}H\mathrm{{-}CN}$ of PAN (at 3.15 ppm) and to $\mathrm{C_6}H_5\mathrm{{-}CH{-}CH_2}$ of PS (at 7.7−6.4 ppm) (see experimental section in Supporting Information, Figure 2): PVAc(20400)-*b*-PAN(4100)-*b*-PS(28400).

Table 1. Synthesis of PVAc-*b*-PAN-*b*-PX Triblock Copolymers by NMP Using a PVAc(20.4K)-*b*-PAN(4.8K)-SG1 Diblock Prepared by CMRP

	block PX		PVAc-*b*-PAN-*b*-PX triblock copolymer	
monomer X	$M_{\mathrm{n,exp\ NMR}}$ (g/mol)^d	$M_{\mathrm{n,th}}$ (g/mol)^e	$M_{\mathrm{n,SEC}}$ (g/mol)^f	M_w/M_n^{f}
Sty^a	28 400	34 000	131 600	1.31
n-BuA^b	23 400	22 300	110 000	1.19
4-VP^c	21 400	24 300	99 000	1.18

^{a} $[\mathrm{Sty}]_0/[\mathrm{PVAc}\text{-}b\text{-}\mathrm{PAN}\text{-}\mathrm{SG1}]_0$ = 435, Sty/DMF = 1/1 (v/v), 120 °C, 5.5 h, conversion = 75%. ^{b} $[n\text{-}\mathrm{BuA}]_0/[\mathrm{PVAc}\text{-}b\text{-}\mathrm{PAN}\text{-}\mathrm{SG1}]_0$ = 205, *n*-BuA/DMF = 1/2.5 (v/v), 120 °C, 2.5 h, conversion = 83%. ^{c} $[4\text{-}\mathrm{VP}]_0/[\mathrm{PVAc}\text{-}b\text{-}\mathrm{PAN}\text{-}\mathrm{SG1}]_0$ = 925, 4-VP/DMF = 1/1 (v/v), 100 °C, 4 h, conversion = 25%. ^{d} Experimental number-average molecular weight determined by ^{1}H NMR in DMSO-d_6. ^{e} Theoretical number-average molecular weight calculated based on the monomer conversion and the initial monomer/macroinitiator molar ratio. ^{f} Number-average molecular weight determined by SEC in DMF (containing 0.025 M LiBr) with polystyrene calibration.

When the same procedure was applied to *n*-butyl acrylate (nBuA), the polymerization was uncontrolled as assessed by a multimodal SEC chromatogram of the copolymer and a broad polydispersity (M_w/M_n = 2.63, results not shown). It has already been established that, for controlling efficiently the acrylate polymerization depending on the nature of alkoxyamine,[6,8,34] a slight excess of free nitroxide compared to the alkoxyamine has to be used in order to decrease the polymerization rate of the acrylate. After optimization of the polymerization procedure, 85% monomer conversion was obtained after 2.5 h of polymerization (see Figure S2 in Supporting Information), and a PVAc(20400)-*b*-PAN(4800)-*b*-PnBuA(23400) was produced with a narrow polydispersity (M_w/M_n = 1.19; Figure 1B) at 120 °C when 1 mol % SG1 was used compared to the starting diblock copolymer. The small shoulder at the high molecular weight side of the SEC chromatogram of the copolymer is attributed to some coupling reactions that were occurring at high conversion. Some tailing is also observed at the low molecular weight side of the SEC chromatogram, probably coming from the occurrence of some transfer reactions that cannot be excluded when the NMP of nBuA using SG1 is concerned.[38]

Finally, the polymerization of 4-vinylpyridine (4VP) was considered at 100 °C without free SG1. In these conditions, the PVAc-*b*-PAN-SG1 initiated the polymerization of 4VP in a controlled manner. The SEC chromatogram shifted toward the higher molecular weight side, while the polydispersity remained narrow (M_w/M_n = 1.18) (see Figure 1C). In the polymerization conditions studied, 25% monomer conversion was reached after 4 h at 100 °C. Comparison of the intensities of the ^{1}H NMR signals corresponding to $\mathrm{CH_2{-}C}H\mathrm{{-}OCOCH_3}$ of PVAc (at 4.82 ppm), $\mathrm{CH_2{-}C}H\mathrm{{-}CN}$ of PAN (at 3.15 ppm), and $\mathrm{C_5}H_4\mathrm{N{-}CH{-}CH_2}$ of PS (at 6.6 ppm) allowed to calculate the molecular weight of each block: PVAc(20400)-*b*-PAN(4800)-*b*-P4VP(21400). ^{13}C NMR spectra of PVAc-*b*-PAN-SG1 and the three triblock copolymers prepared in this work are presented in the Supporting Information (Figure S4).

In summary, acrylonitrile polymerization initiated by CMRP from a PVAc−Co(acac)$_2$ precursor was stopped by addition of SG1. A rapid cobalt/nitroxide exchange reaction occurred with formation of PVAc-*b*-PAN diblock copolymer end-capped by SG1 (PVAc-*b*-PAN-SG1). The C−ON bond of the newly formed

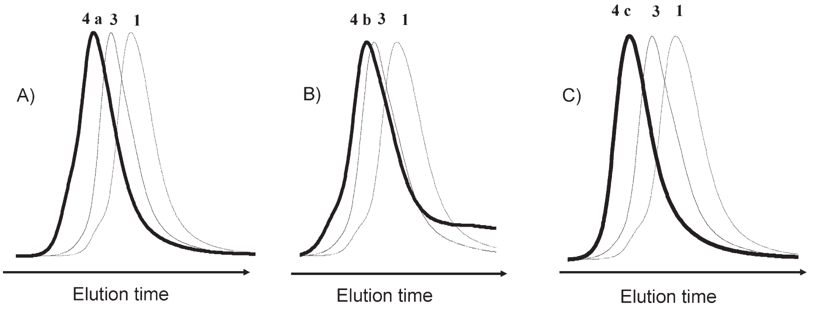


Figure 1. Overlay of SEC chromatograms for PVAc−Co(acac)$_2$ **1** (dotted line, M_n = 53 100 g/mol, M_w/M_n = 1.22), PVAc-*b*-PAN-SG1 **3** (full line, M_n=78 600 g/mol, M_w/M_n=1.20) and (A) PVAc-*b*-PAN-*b*-PS **4a** (bold line, M_n=131 600 g/mol, M_w/M_n=1.31), (B) PVAc-*b*-PAN-*b*-PnBuA **4b** (bold line, M_n=110 000 g/mol, M_w/M_n=1.19), and (C) PVAc-*b*-PAN-*b*-P4VP **4c** (bold line, M_n=99 000 g/mol, M_w/M_n=1.18). M_n are determined by SEC in DMF (containing 0.025 M LiBr) with polystyrene calibration.

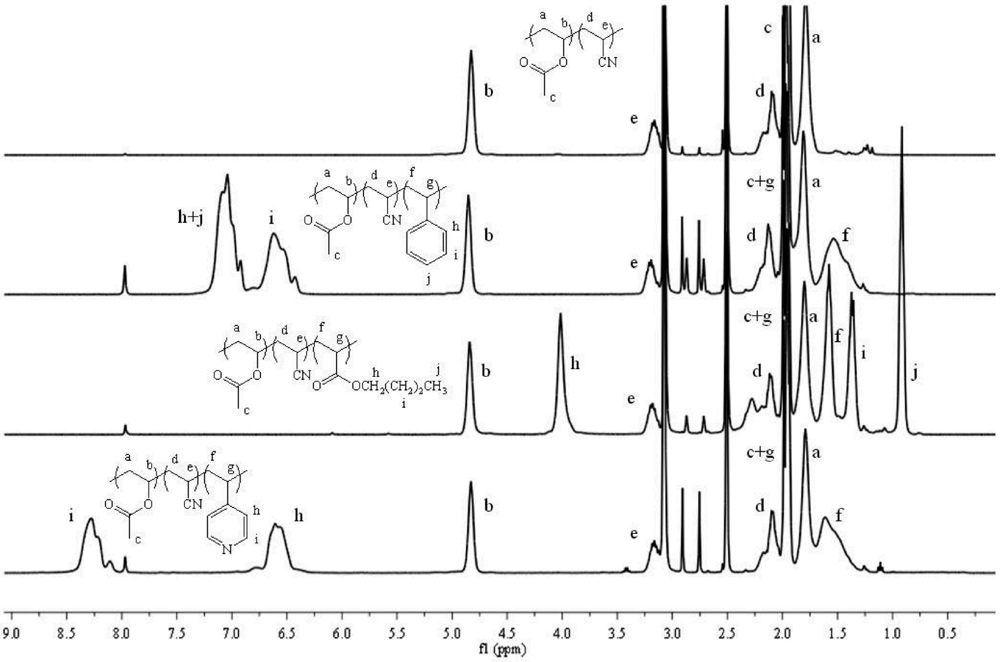


Figure 2. ^{1}H NMR (400 MHz, 353 K, DMSO-d_6) of PVAc-*b*-PAN-SG1, PVAc-*b*-PAN-*b*-PS, PVAc-*b*-PAN-*b*-PnBuA, and PVAc-*b*-PAN-*b*-P4VP. PVAc, PAN, PS, PnBuA, P4VP, and SG1 stand for poly(vinyl acetate), poly(acrylonitrile), poly(styrene), poly(*n*-butyl acrylate), poly(4-vinylpyridine), and *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl, respectively.

macroalkoxyamine was easily reactivated under heating to initiate the nitroxide-mediated polymerization of various vinyl monomers such as styrene, *n*-butyl acrylate, and 4-vinylpyridine whose polymerization cannot be controlled up to now by CMRP. Novel well-defined ABC triblock copolymers were thus produced by combination of CMRP and NMP techniques. To our knowledge, this strategy is a unique tool for precise design of such triblock copolymers based on conjugated and nonconjugated monomers. Our approach is thus complementary to other efficient techniques that allow the controlled synthesis of other types of block copolymers based also on conjugated and nonconjugated monomers.[39−41]

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Supporting Information Available: Experimental procedures and characterizations on prepared (co)polymers. This material is free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987–2988.
(2) Detrembleur, C.; Sciannamea, V.; Koulic, C.; Claes, M.; Hoebeke, M.; Jerome, R. *Macromolecules* **2002**, *35*, 7214–7223.
(3) Detrembleur, C.; Teyssie, P.; Jerome, R. *Macromolecules* **2002**, *35*, 1611–1621.
(4) Sciannamea, V.; Jerome, R.; Detrembleur, C. *Chem. Rev.* **2008**, *108*, 1104–1126.
(5) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245–5254.
(6) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904–3920.
(7) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661–3688.
(8) Chauvin, F.; Dufils, P.-E.; Gigmes, D.; Guillaneuf, Y.; Marque, S. R. A.; Tordo, P.; Bertin, D. *Macromolecules* **2006**, *39*, 5238–5250.
(9) Clement, B.; Trimaille, T.; Alluin, O.; Gigmes, D.; Mabrouk, K.; Feron, F.; Decherchi, P.; Marqueste, T.; Bertin, D. *Biomacromolecules* **2009**, *10*, 1436–1445.
(10) Phan, T. N. T.; Bertin, D. *Macromolecules* **2008**, *41*, 1886–1895.

(11) Dire, C.; Charleux, B.; Magnet, S.; Couvreur, L. *Macromolecules* **2007**, *40*, 1897–1903.

(12) Drockenmuller, E.; Catala, J.-M. *Macromolecules* **2002**, *35*, 2461–2466.

(13) Knoop, C. A.; Studer, A. *J. Am. Chem. Soc.* **2003**, *125*, 16327–16333.

(14) Wetter, C.; Gierlich, J.; Knoop, C. A.; Müller, C.; Schulte, T.; Studer, A. *Chem.—Eur. J.* **2004**, *10*, 1156–1166.

(15) Nicolas, J.; Dire, C.; Mueller, L.; Belleney, J.; Charleux, B.; Marque, S. R. A.; Bertin, D.; Magnet, S.; Couvreur, L. *Macromolecules* **2006**, *39*, 8274–8282.

(16) Detrembleur, C.; Claes, M.; Jerome, R. *ACS Symp. Ser.* **2003**, *854*, 496–518.

(17) Guillaneuf, Y.; Gigmes, D.; Marque, S. R. A.; Astolfi, P.; Greci, L.; Tordo, P.; Bertin, D. *Macromolecules* **2007**, *40*, 3108–3114.

(18) Nicolas, J.; Couvreur, P.; Charleux, B. *Macromolecules* **2008**, *41*, 3758–3761.

(19) Greene, A. C.; Grubbs, R. B. *Macromolecules* **2009**, *42*, 4388–4390.

(20) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363–370.

(21) Grubbs, R. B.; Wegrzyn, J. K.; Xia, Q. *Chem. Commun.* **2005**, 80–82.

(22) Lutz, J.-F.; Lacroix-Desmazes, P.; Boutevin, B.; Le Mercier, C.; Gigmes, D.; Bertin, D.; Tordo, P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **2002**, *43*, 287–288.

(23) Debuigne, A.; Caille, J.-R.; Detrembleur, C.; Jerome, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3439–3442.

(24) Debuigne, A.; Caille, J.-R.; Jerome, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1101–1104.

(25) Debuigne, A.; Poli, R.; Jerome, C.; Jerome, R.; Detrembleur, C. *Prog. Polym. Sci.* **2009**, *34*, 211–239.

(26) Kaneyoshi, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 2757–2763.

(27) Debuigne, A.; Willet, N.; Jerome, R.; Detrembleur, C. *Macromolecules* **2007**, *40*, 7111–7118.

(28) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944.

(29) Debuigne, A.; Champouret, Y.; Jerome, R.; Poli, R.; Detrembleur, C. *Chem.—Eur. J.* **2008**, *14*, 7623–7637.

(30) Debuigne, A.; Warnant, J.; Jerome, R.; Voets, I.; de Keizer, A.; Cohen Stuart, M. A.; Detrembleur, C. *Macromolecules* **2008**, *41*, 2353–2360.

(31) Debuigne, A.; Caille, J.-R.; Jerome, R. *Macromolecules* **2005**, *38*, 5452–5458.

(32) Debuigne, A.; Caille, J.-R.; Willet, N.; Jerome, R. *Macromolecules* **2005**, *38*, 9488–9496.

(33) Marque, S. *J. Org. Chem.* **2003**, *68*, 7582–7590.

(34) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5929–5939.

(35) Diaz, T.; Fischer, A.; Jonquieres, A.; Brembilla, A.; Lochon, P. *Macromolecules* **2003**, *36*, 2235–2241.

(36) Schierholz, K.; Givehchi, M.; Fabre, P.; Nallet, F.; Papon, E.; Guerret, O.; Gnanou, Y. *Macromolecules* **2003**, *36*, 5995–5999.

(37) Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromol. Rapid Commun.* **2004**, *25*, 1215–1220.

(38) Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. *Macromolecules* **2002**, *35*, 4912–4918.

(39) Ray, B.; Kotani, M.; Yamago, S. *Macromolecules* **2006**, *39*, 5259–5265.

(40) Yamago, S.; Kayahara, E.; Kotani, M.; Ray, B.; Kwak, Y.; Goto, A.; Fukuda, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 1304–1306.

(41) Nicolaÿ, R.; Kwak, Y.; Matyjaszewski, K. *Chem. Commun.* **2008**, 5336–5338.