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Nitroxide-mediated polymerization of methacrylates in the presence of 4-vinyl  
pyridine as controlling comonomer

*X. G. Qiao,<sup>1,2,3</sup> Z. Zhou,<sup>2</sup> X. C. Pang,<sup>3</sup> M. Lansalot,<sup>1</sup> E. Bourgeat-Lami<sup>1\*</sup>*

1. University of Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Novembre 1918, F-69616 Villeurbanne, France.
2. College of Chemistry and Chemical Engineering, and Henan Key laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, China.
3. School of Material Science and Engineering, Zhengzhou University, Zhengzhou, P. R. China.

**ABSTRACT.** The controlled polymerization of methacrylic monomers by nitroxide-mediated polymerization (NMP) still represents a challenge in polymer science. This issue can be circumvented by the addition of a small amount of a comonomer known to exhibit a controlled character in NMP, the most representative example being styrene. The purpose of this work is to explore the use of 4-vinyl pyridine (4VP) as controlling comonomer, while conferring at the same time some functionality to the polymer chains. The NMP of methyl methacrylate (MMA), poly(ethylene glycol) methyl ether methacrylate (PEOMA<sub>950</sub>,  $M_n = 950 \text{ g mol}^{-1}$ ) and methacrylic acid (MAA) using a small amount of 4VP under mild experimental conditions ( $< 90 \text{ }^\circ\text{C}$ , atmospheric pressure), was investigated in this work. The copolymerization of MMA or PEOMA<sub>950</sub> with 10 mol% 4VP, mediated by the use of the BlocBuilder® alkoxyamine and a small amount of free nitroxide SG1, exhibited all the features of a controlled system in agreement with the favored incorporation of 4VP at the chain ends, leading to an efficient deactivation of the propagating radicals by the nitroxide SG1. In contrast, the polymerization of MAA was uncontrolled in the same conditions likely due to acid/base interaction between MAA and 4VP, affecting the reactivity of the functional comonomer. Consistently, the copolymerization of MAA with MMA also led to a progressive loss of control as the MAA content in the feed was increased. Among all the polymers synthesized, the P(MMA<sub>72-co-4VP</sub><sub>10</sub>)-SG1 macroalkoyamine was then successfully used to reinitiate the copolymerization of *n*-butyl methacrylate (BMA) and 4VP both in solution and via dispersion polymerization in a mixture of ethanol and water. Finally, raspberry-like polymer/silica composite particles were prepared through nitroxide-mediated dispersion polymerization performed in the presence of silica nanoparticles, taking benefit of the strong acid-base interaction between 4VP and silica.

**Keywords:** Nitroxide-mediated polymerization, 4-vinyl pyridine, methacrylate, copolymerization, dispersion polymerization, silica, composite particles

## INTRODUCTION

After more than 30 years of research and development, nitroxide-mediated polymerization (NMP) has gained considerable ground against other reversible-deactivation radical polymerization processes and is now recognized as one of the most powerful living radical polymerization techniques.<sup>1</sup> NMP has not only gained in efficiency and robustness over the last few years making it now possible to access a variety of polymer architectures such as block copolymers or star polymers,<sup>2,3</sup> but its fields of applications have also significantly expanded to include additives for pigments,<sup>4</sup> nanoporous materials,<sup>5</sup> bioconjugates,<sup>6</sup> micro/optoelectronic devices,<sup>7</sup> and electrolytes for lithium-metal batteries.<sup>8</sup>

Historically, the early NMP systems relied on the use of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) as nitroxide, and were limited to the polymerization of styrene and its derivatives at relatively high reaction temperatures (typically > 120 °C).<sup>9,10,11</sup> A major breakthrough was achieved with the development of the so-called second generation nitroxides like 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO)<sup>12</sup> and *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] (SG1), and related alkoxyamines<sup>13</sup> which enabled the polymerization to be conducted at much lower temperatures and to extend the range of monomers to acrylates, acrylamides, and dienes.<sup>2</sup> This has opened up entirely new perspectives and notably the possibility of working in dispersed media such as in aqueous emulsion or miniemulsion.<sup>14</sup>

Despite these substantial progresses, nitroxide-mediated homopolymerization of methacrylic esters such as methyl methacrylate (MMA) and its derivatives has long represented a challenge in polymer science<sup>15</sup> and it is only recently that this issue was circumvented with the development of new nitroxides.<sup>16,17,18,19</sup> The lack of control was attributed to cross-disproportionation side reactions and to a large activation-deactivation equilibrium constant (K).<sup>2</sup> Various strategies have been explored over time including the implementation

of new polymerization processes,<sup>20,21</sup> and the use of additives.<sup>22,23</sup> Among the different approaches, an efficient strategy first developed by Charleux *et al.*<sup>24,25,26</sup> for SG1-mediated polymerization of MMA consists in the addition of a very small amount of styrene (St) leading to a strong reduction of the equilibrium constant. The key role of the styrenic monomer was explained by the formation of macroalkoxyamines with a single terminal styrenic unit attached to the nitroxide. Moreover, because of the penultimate methacrylate subunits, an enhanced dissociation rate and thus a lower temperature of dissociation (70 – 90 °C) were achieved. The comonomer approach was extended with success to a variety of styrenic derivatives including 4-styrene sulfonate,<sup>27,28</sup> pentafluorostyrene,<sup>29</sup> and 9-(4-vinylbenzyl)-9H-carbazole,<sup>30</sup> as well as to numerous methacrylates, such as methacrylic acid (MAA),<sup>27,31</sup> benzyl methacrylate,<sup>32</sup> and poly(ethylene glycol) methyl ether methacrylate (PEOMA).<sup>33,34</sup> This not only led to controlled polymerizations but the controlling comonomer also enabled to impart some functionalities to the polymer chains. However, to the best of our knowledge, no similar study had ever been conducted on 4-vinyl pyridine (4VP).

In this study, 4VP is investigated as controlling comonomer for the NMP of methacrylic esters, namely MMA and PEOMA<sub>950</sub> ( $M_n = 950 \text{ g mol}^{-1}$ ), and for the synthesis of PMAA and MAA/MMA copolymers under mild experimental conditions (< 90 °C, atmospheric pressure). Pyridine-containing polymers have unique physical properties and are indeed highly attractive in materials science. The control of the polymerization and the polymerization kinetics were investigated in details. One of the resulting macroalkoxyamines, P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1, was then used to reinitiate the copolymerization of *n*-butyl methacrylate (BMA) with 4VP both in bulk and in an hydroalcoholic medium via dispersion polymerization, leading to the formation of block copolymers. Moreover, nitroxide-mediated dispersion polymerization was also carried out in the presence of silica nanoparticles to form

composite particles relying on the strong acid-base interaction between the 4VP units and the silica sol.

## EXPERIMENTAL SECTION

### Materials.

The *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) alkoxyamine initiator (BlocBuilder<sup>®</sup>, 99%) and *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1, 85%) were kindly supplied by Arkema. Poly(ethylene oxide) methyl ether methacrylate (PEOMA<sub>950</sub>,  $M_n = 950 \text{ g mol}^{-1}$ , Aldrich), methyl methacrylate (MMA, 99%, Aldrich), *n*-butyl methacrylate (BMA, 99%, Aldrich) and 4-vinyl pyridine (4VP, 95%, Aldrich) were used without any further purification. Dimethyl sulfoxide (DMSO,  $\geq 99\%$ , Aldrich), 1,3,5-trioxane ( $\geq 99\%$ , Aldrich) and ethanol (EtOH, Prolabo, pure) were used as received. DMSO- $d_6$  ( $\geq 99\%$ , Aldrich) was used as solvent for NMR. Deionized water (Purelab Classic UV, ElgaLab Water) was used for all experiments. The silica sol ( $D_n = 22 \text{ nm}$  and  $D_w/D_n = 1.01$ , Figure S4) was synthesized using a biphasic L-arginine catalyzed process as reported elsewhere.<sup>35</sup>

### SG1-mediated copolymerization of methacrylic monomers and 4VP at 80 °C in DMSO

In a typical example (MV01 in Table 1), SG1 (0.018 g, 0.06 mmol), MMA (5.1 g, 51.0 mmol) and 4VP (0.61 g, 5.8 mmol) were first dissolved in DMSO (17 mL). 1,3,5-trioxane (0.01 g, 0.6 mmol) was then added as internal standard for NMR analysis. The solution was introduced into a 50 mL three-neck round-bottom flask, and degassed with nitrogen bubbling for 20 min. The BlocBuilder<sup>®</sup> alkoxyamine (0.21 g, 0.55 mmol) was then introduced into the flask, followed by nitrogen bubbling for another 10 min. The mixture was heated to 80 °C and the time zero of the polymerization was taken when the reaction temperature reached

75 °C. Samples were collected periodically, dissolved either in DMSO-d<sub>6</sub> to be analyzed by proton NMR spectroscopy to determine the conversion by comparing the integral of the 1,3,5-trioxane peak to those of the vinylic protons of the monomers, or in THF for size exclusion chromatography (SEC) to determine the number-average ( $M_n$ ) and weight-average ( $M_w$ ) molar masses, and dispersity  $D = M_w/M_n$ . The copolymerization reaction was then reproduced at a larger scale (10-fold increase) and stopped after 1.5 h to get a larger amount of polymer that was also analyzed by SEC and <sup>1</sup>H NMR (MMA and 4VP conversions were, respectively, 53.9 and 69.6 mol%). The average number of comonomer units within the chains was determined by using  $M_n$  from SEC and the average composition of the copolymer from NMR. The final product P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 ( $M_n = 8300 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.2$ ) was dried under vacuum after precipitation in diethyl ether, and stored in the fridge before use. Conditions of all the solution polymerization experiments are listed in Table 1.

#### **Chain extension of P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 macroalkoxyamine initiator in DMSO**

Chain extension of the SG1-capped P(MMA<sub>72-co</sub>-4VP<sub>10</sub>) macroinitiator was performed in DMSO at 85 °C. BMA (5.0 g, 5.88 mol L<sup>-1</sup>) and 4VP (0.35 g, 0.56 mol L<sup>-1</sup>) were mixed with 0.2 g of macroalkoxyamine (4.03 mmol L<sup>-1</sup>) and introduced in a 50 mL three-neck round-bottom flask with 15 mL of DMSO and 0.01 g of 1,3,5-trioxane. The reaction was performed at 85 °C for 1.75 h, after nitrogen bubbling for 30 min in an ice bath. Time zero of the polymerization was taken when the reaction temperature reached 70 °C. Samples were periodically withdrawn to follow the evolution of monomer conversion by NMR and of molar masses by SEC.

### **Chain extension of P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 macroalkoxyamine initiator with a mixture of BMA and 4VP at 85 °C in hydro-alcoholic medium with and without silica**

Dispersion polymerization of BMA and 4VP using P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 as macroinitiator was performed in an acidic EtOH/H<sub>2</sub>O (1/9 v/v) mixture. For the blank polymerization without silica, the macroalkoxyamine (0.3 g, 2.81 mmol L<sup>-1</sup>) was first dissolved into 10 g of the hydro-alcoholic medium at pH = 2, and kept overnight in the fridge (5 °C). The mixture was then introduced into a 50 mL three-neck round-bottom flask placed in an ice bath, and degassed by nitrogen bubbling for 30 min after addition of BMA (2.5 g, 1.35 mol L<sup>-1</sup>) and 4VP (0.18 g, 0.13 mol L<sup>-1</sup>). The reaction was performed at 85 °C for 5 h. Samples were taken periodically to determine the monomer conversion by gravimetric analysis and the molar mass and molar mass distributions by SEC. The same method was used for the dispersion polymerization experiment performed in the presence of silica, except that after the addition of BMA and 4VP, 2 mL of the aqueous silica sol ([SiO<sub>2</sub>] = 30 g L<sup>-1</sup>) was introduced in the suspension medium, and the mixture sonicated for 2 minutes to form a homogeneous dispersion with a pH of 6.3. To keep the initial macroalkoxyamine concentration and the total volume of the dispersion medium the same as in the blank experiment, 2 mL of the water used to dissolve the macroalkoxyamine was subtracted from the initial 10 g of the hydro-alcoholic mixture. As previously, the polymerization was carried out at 85 °C after nitrogen bubbling for 30 min.

### **Characterization techniques**

<sup>1</sup>H NMR spectroscopy for kinetic studies was performed using a Bruker DRX 300 spectrometer. The individual monomer conversions  $X_{\text{mol}}$  were directly accessible by the NMR analyses. SEC analyses of the MMA-, MAA- and MMA/MMA-based macroalkoxyamines were performed in THF (Viscotek TDA305 equipped with a refractive index detector) using a



flow rate of 1 mL min<sup>-1</sup>. All polymers were injected at a concentration of 2 mg mL<sup>-1</sup>, after filtration through a 0.45 μm pore-size membrane. The separation was carried out on three Polymer Laboratories columns [3 × PLgel 5 μm Mixed C (300 × 7.5 mm)] and a guard column (PL gel 5 μm). Columns and detectors were maintained at 40 °C. SEC analyses for PEOMA-based macroalkoxyamines and copolymers from dispersion polymerization were performed in DMF (EcoSEC semi-micro GPC system from Tosoh equipped with a dual flow refractive index detector and a UV detector) at 50 °C with a flow rate of 1 mL min<sup>-1</sup>. All polymers were injected at a concentration of 2 mg mL<sup>-1</sup>, after filtration through a 0.45 μm pore-size membrane. Separation was performed with a guard column and three PSS GRAM columns (7 μm, 300 × 7.5 mm). In all cases, the average molar masses ( $M_w$  and  $M_n$ ) and molar mass distributions ( $M_w/M_n$ ) were calculated with a calibration curve based on PMMA standards. Prior to SEC analysis, the MAA-containing polymers were methylated using tri(methylsilyl) diazomethane as reported elsewhere.<sup>36</sup>

The hydrodynamic diameter ( $Z_{av}$ , nm) and the dispersity of the samples (indicated by the PDI value; the higher this value, the broader the size distribution) were measured by dynamic light scattering (DLS) using the Nano ZS Instrument from Malvern. In a typical experiment, one drop of the suspension was diluted in water and the data were collected at 173° scattering angle using the fully automatic mode of the Zetasizer system.

Transmission electron microscopy (TEM) analysis of the composite latex particles was performed using a Philips CM120 transmission electron microscope at an accelerating voltage of 80 kV (Centre Technologique des Microstructures, platform of Université Claude Bernard Lyon 1, Villeurbanne, France). The diluted sample was dropped on a Formvar-carbon coated copper grid and dried under air before observation. Phosphotungstic acid (1.5 wt %, pH = 7) was used to increase the specimen contrast in the case of the blank latex synthesized in the absence of silica.

**Table 1.** Experimental conditions used for the copolymerization of methacrylic monomers with a low percentage of 4VP in DMSO at 80 °C.

No	[MMA] (mol L <sup>-1</sup> )	[PEOMA <sub>950</sub> ] (mol L <sup>-1</sup> )	[MAA] (mol L <sup>-1</sup> )	[4VP] (mol L <sup>-1</sup> )	[SG1] (mol L <sup>-1</sup> )	[BlocBuilder <sup>®</sup> ] (mol L <sup>-1</sup> )	$f_{0,4VP}$ <sup>a</sup>	Target $M_n$ (at 100% conversion)
MV01	2.21	/	/	0.252	$2.7 \times 10^{-3}$	0.024	0.102	10700
MV02	/	0.324	/	0.036	$1.2 \times 10^{-3}$	0.010	0.100	30500
MV03	/	/	2.85	0.386	$4.1 \times 10^{-3}$	0.037	0.118	9200
MV04	2.65	/	0.29	0.34	$5.2 \times 10^{-3}$	0.033	0.104	10300
MV05	1.52	/	1.55	0.35	$5.3 \times 10^{-3}$	0.034	0.102	9900
MV06	0.81	/	2.45	0.34	$5.2 \times 10^{-3}$	0.033	0.095	10300

<sup>a</sup> Initial molar fraction of 4VP in the feed.

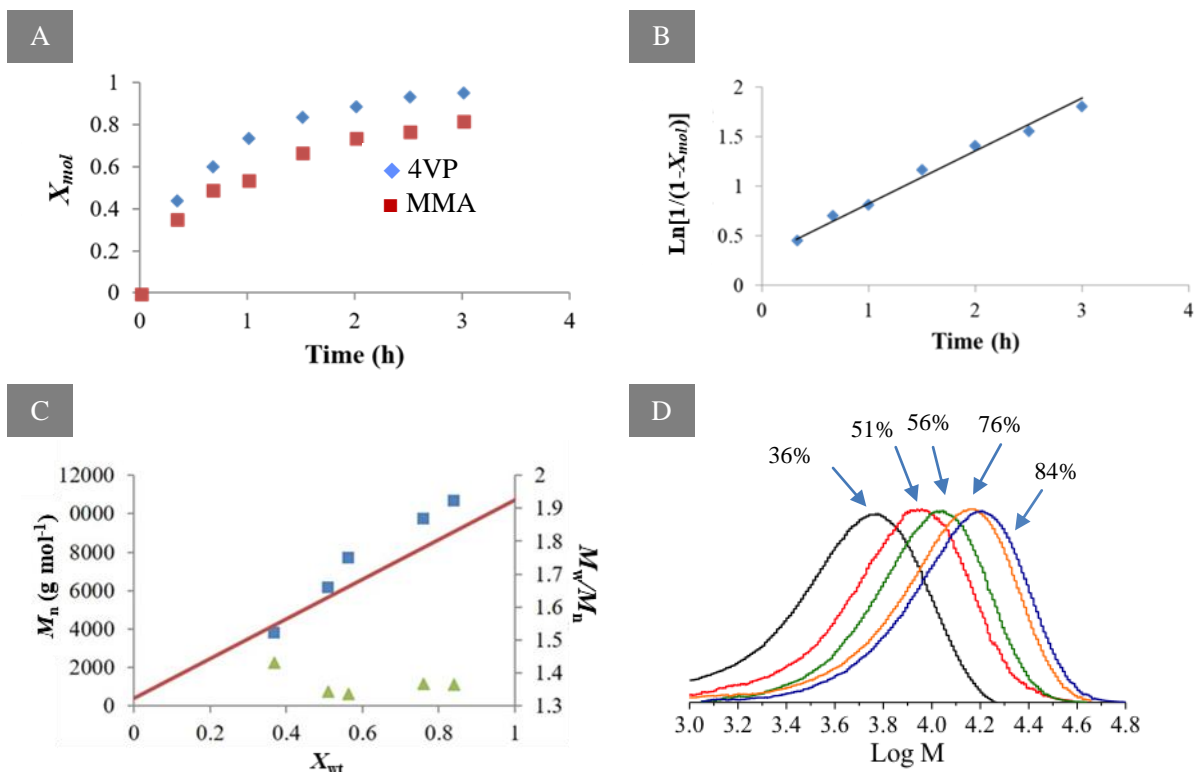
## RESULTS AND DISCUSSION

The incorporation of vinyl pyridine into polymer chains has attracted tremendous attention in the literature due to the unique properties of the resulting products. 4VP has been successfully polymerized by reversible-deactivation radical polymerization, including ATRP,<sup>37</sup> RAFT<sup>38</sup> and NMP using TEMPO,<sup>39,40,41</sup> 4-hydroxy-TEMPO,<sup>42</sup> TIPNO,<sup>43,44,45</sup> SG1<sup>46,47,48,49</sup> or derived alkoxyamines, as controlling agents. 4VP has also been incorporated into block copolymers,<sup>50,51,52</sup> and copolymerized with styrene<sup>41,45</sup> or acrylonitrile,<sup>49</sup> but to the best of our knowledge, it has never been investigated as a comonomer to control the NMP of methacrylates. Given the structural similarities between 4VP and St, our purpose in the following section is thus to establish whether 4VP could be a suitable controlling comonomer, and at the same time confer some functionality to the resulting polymer chains.

### *Copolymerization of methacrylic monomers with a low amount of 4VP*

All the copolymerization reactions were performed in DMSO at 80 °C using the BlocBuilder<sup>®</sup> as initiator in the presence of small percentage of free SG1 (11-15 mol% with respect to BlocBuilder<sup>®</sup>), according to the procedure previously established in the literature for the copolymerization of MMA with St.<sup>25</sup> The initial molar fraction of 4VP in the feed was fixed at 10 mol% for all the polymerizations, and MMA, PEOMA<sub>950</sub>, MAA and mixtures of MAA and MMA were investigated as methacrylic monomers in this work (see Table 1 for details). The first experiment performed was MMA/4VP copolymerization (MV01, Table 1). A favored incorporation of the controlling comonomer since the beginning of the reaction is key in ensuring an efficient deactivation of the propagating radicals by the nitroxide SG1 and a low K value, as previously reported for MMA/St copolymerization.<sup>24</sup> As shown by the evolution of individual monomer conversions with time in [Figure 1A](#), 4VP is consumed faster than MMA indicating a preferential incorporation of the vinylic monomer into the

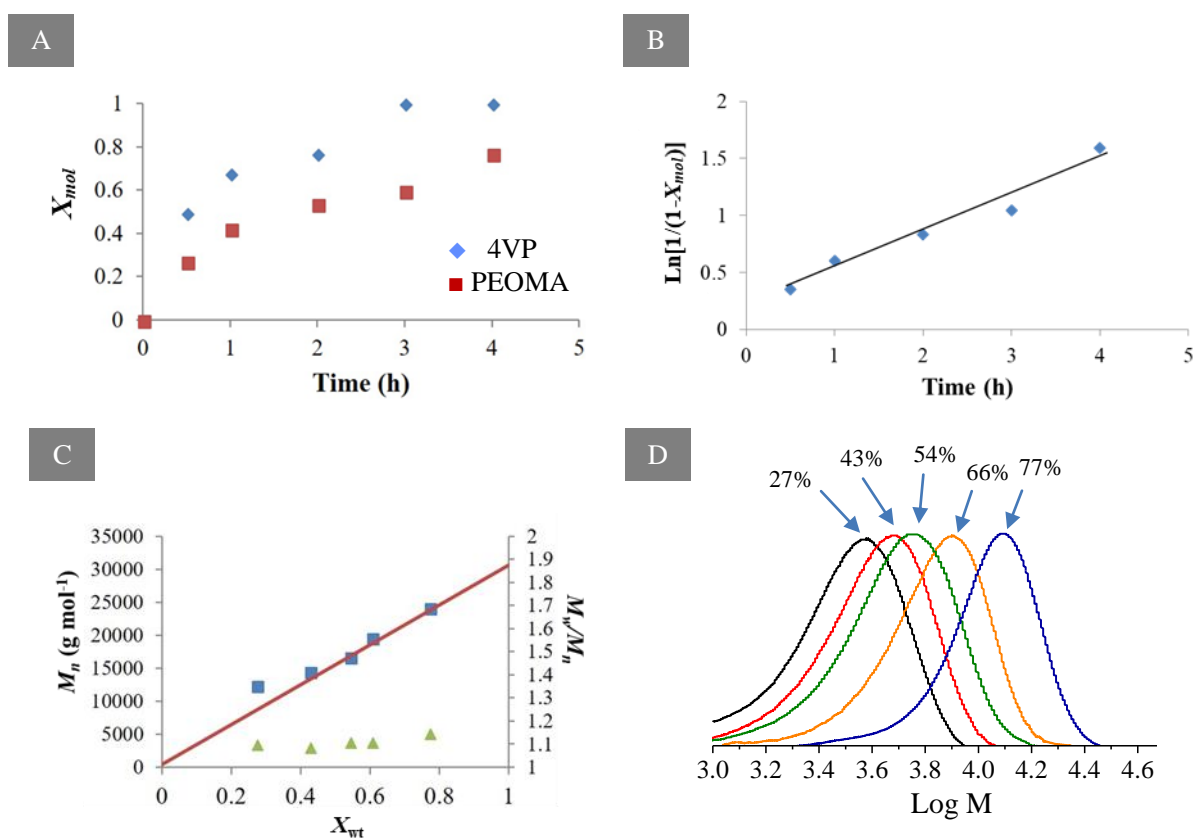
polymer chains in agreement with the monomer reactivity ratios.<sup>53</sup> Indeed, according to Tamikado, the reactivity of 4VP is very close to that of styrene: the  $r_1$  value (with monomer 1 = MMA) is comparable (0.46 for St vs. 0.57 for 4VP), while the  $r_2$  value is slightly higher (0.52 for St and 0.79 for 4VP). Besides Abdul Rahim *et al.*<sup>48</sup> have recently reported the NMP of 4VP in solution at 110 °C using BlocBuilder<sup>®</sup> as initiator and showed that the polymerization was well controlled, highlighting again the similitude between 4VP and St. It seems thus reasonable to assume that 4VP can act as an efficient controlling comonomer for the NMP of methacrylic esters. The polymerization indeed showed all the characteristics of a controlled system. The linear evolution of the semilogarithmic kinetics plot of  $\ln[1/(1-X_{\text{mol}})]$  vs time indicates first-order kinetics with respect to monomers and a constant concentration of propagating radicals (Figure 1B). The evolution of  $M_n$  as a function of the weight conversion (Figure 1C) shows a linear increase, and the molar mass distributions remain narrow throughout the polymerization ( $M_w/M_n < 1.4$ ), indicating a good control of the polymerization even though the experimental  $M_n$  were slightly higher than the theoretical values at high conversion, suggesting the occurrence of irreversible termination reactions. The shift of the SEC traces toward higher molar masses nevertheless confirmed the living character of the polymerization (Figure 1D). A larger amount of macroalkoxyamine was thus prepared in the same conditions by stopping the reaction after 1.5 h, resulting in polymer chains with a low dispersity ( $M_n = 8300 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.2$ ) (Figure S1, Supporting Information) containing on average 72 MMA and 10 4VP units, hereafter denoted as P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1. The MMA and 4VP conversions determined after removal of the residual monomer by precipitation (53.9 and 69.6 mol%, respectively), agreed well with the ones obtained in the kinetic study, although they were slightly lower likely due to a scaling effect. The resulting polymer was set aside for further use in chain extension reactions.



**Figure 1.** Copolymerization of MMA with 11 mol% 4VP in DMSO at 80 °C in the presence of 10 mol% of free SG1 based on the BlocBuilder® initiator content (MV01 in Table 1). A) Individual monomer conversions ( $X_{mol}$ ) and B)  $\text{Ln}[1/(1-X_{mol})]$  vs time, and C)  $M_n$  (■),  $M_w/M_n$  (▲) (determined by SEC in THF, PMMA calibration) and D) size exclusion chromatograms vs weight conversion. The black straight line in the  $\text{Ln}[1/(1-X_{mol})]$  vs time plot is a guide for the eye. The red straight line in the  $M_n$  vs  $X_{wt}$  plot corresponds to the theoretical evolution.

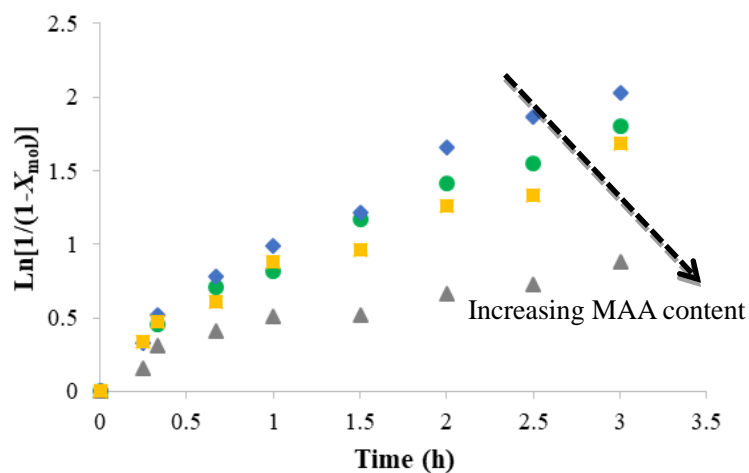
As seen in Figure 2, very similar results were obtained for the copolymerization of PEOMA<sub>950</sub> with 4VP (MV02, Table 1). A favored incorporation of 4VP since the beginning of the copolymerization is again observed, enabling an efficient deactivation of the propagating radicals by the SG1 nitroxide and a good control of the polymerization up to high conversions. The  $M_n$  values were even closer to the theoretical line and the molar mass distribution narrower ( $M_w/M_n < 1.2$ ). The living character of the polymerization was again evidenced by the shift of the SEC peaks towards higher molar masses with increasing

monomer conversion (Figure 2D). A similar quality of control was already reported in the literature for the NMP of PEOMA<sub>950</sub> with a low amount of St,<sup>34</sup> confirming once again that 4VP is as effective as St in controlling the homopolymerization of methacrylate monomers. It can be thus concluded that SG1-mediated copolymerization of MMA or PEOMA<sub>950</sub> with a small percentage of 4VP performed in DMSO at 80 °C exhibits all the characteristics of a controlled radical polymerization.



**Figure 2.** Copolymerization of PEOMA<sub>950</sub> with 10 mol% 4VP in DMSO at 80°C in the presence of 12 mol% free SG1 based on BlocBuilder<sup>®</sup> initiator (MV02 in Table 1). A) Individual monomer conversions ( $X_{mol}$ ) and B)  $\ln[1/(1-X_{mol})]$  vs time, and C)  $M_n$  (■),  $M_w/M_n$  (▲) (determined by SEC in DMF, PMMA calibration) and D) size exclusion chromatograms vs weight conversion. The black straight line in the  $\ln[1/(1-X_{mol})]$  vs time plot is a guide for the eye. The red straight line in the  $M_n$  vs  $X_{wt}$  plot corresponds to the theoretical evolution.

These positive results prompted us to investigate other methacrylic monomers, such as methacrylic acid (MAA). However, attempt to polymerize MAA in the same conditions as for MV01 or MV02, completely failed (MV03, Table 1). As shown in Figure S2 (Supporting Information), the polymerization stopped at very low conversion. To better understand the role of MAA in the course of the polymerization, it was copolymerized with MMA and 4VP, for various MAA to MMA molar ratios (MV04 to MV06, Table 1). The final conversion was directly dependent on the MAA content and decreased with increasing the amount of MAA in the feed (Figure S3, Supporting Information). As seen in Figure 3, the semilogarithmic kinetic plot of  $\ln[1/(1-X_{\text{mol}})]$  vs time was linear for low MAA contents (MV04 and MV05) but tends to curve for higher molar fractions indicating a loss in radical activity resulting in a non first-order kinetics behavior (MV06, MAA/MMA = 3/1, Table 1).

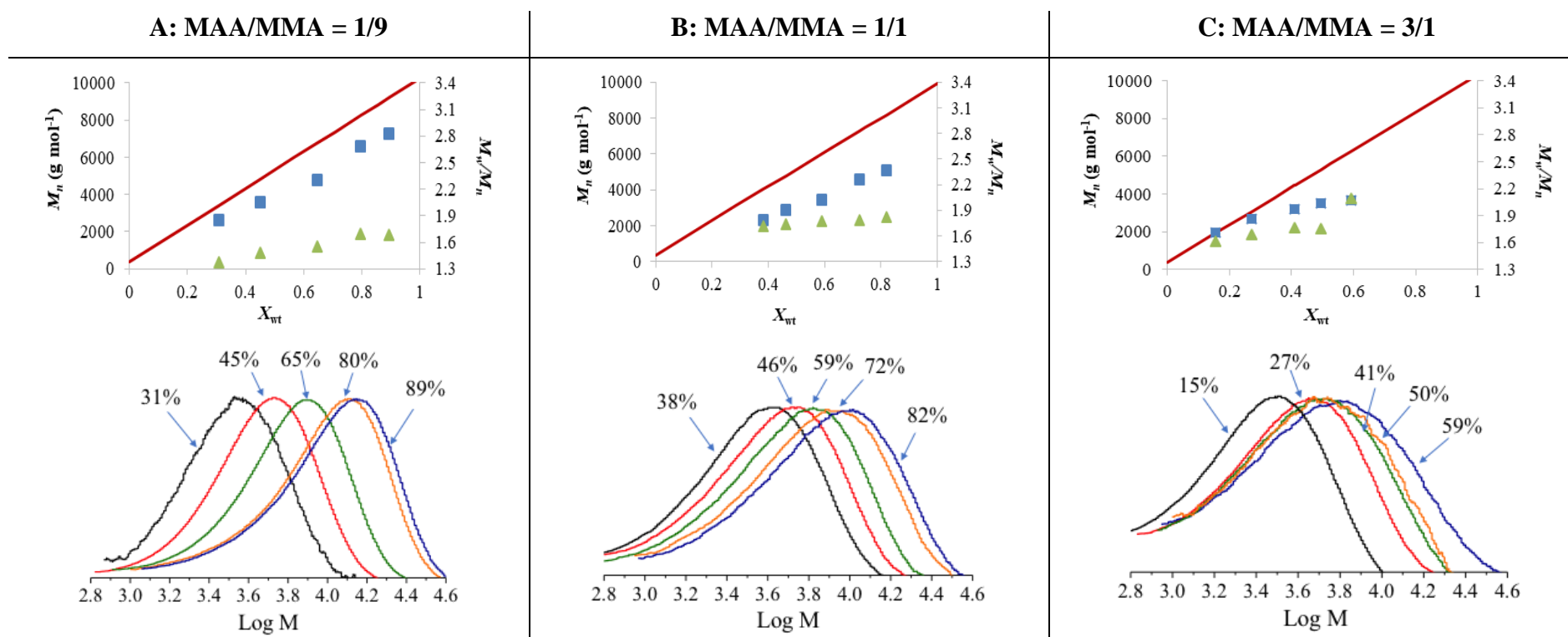


**Figure 3.** Plot of  $\ln[1/(1-X_{\text{mol}})]$  vs time for the copolymerization of MAA with MMA in the presence of 10 mol% 4VP mediated by the BlocBuilder<sup>®</sup> and 15 mol% of free SG1 (based on the initiator) in DMSO at 80 °C for different MAA/MMA molar ratios: MV01 (no MAA, ●), MV04 (MAA/MMA = 1/9, ◆), MV05 (MAA/MMA = 1/1, ■) and MV06 (MAA/MMA = 3/1, ▲).

▲) (Table 1).

Such a plateauing in monomer conversion has already been reported in the literature during the synthesis of PMMA homopolymer (without the addition of Sty) by SG1-mediated polymerization,<sup>25,54</sup> and is an expected behavior in the absence of controlling comonomer. The evolution of  $M_n$  with conversion was also affected by the presence of MAA. While the molar mass evolved linearly with conversion for low MAA contents as expected (Figures 4A and 4B), it leveled up at around 40% conversion for higher MAA contents while the molar mass distributions significantly broadened (Figure 4C). The lower the MAA content, the better was however the control of the polymerization as indicated by the shift of the SEC traces towards lower retention volumes and the absence of residual peak in the low molar mass region for 10 mol% of MAA (MV04, Table 1). These results are completely different from our previous work on the NMP of PEOMA<sub>950</sub> and MAA with a low amount of St for which a very good control was observed even for high MAA contents (> 80 mol%).<sup>55</sup> It is thus clear that 4VP is not a suitable controlling comonomer for the NMP of MAA, which can be tentatively ascribed to acid-base interaction between MAA and the pyridine group of 4VP during the copolymerization.<sup>56</sup> Indeed, such an interaction may significantly influence the reactivity of 4VP and the activation-deactivation equilibrium constant, resulting in a high concentration of propagating radicals favoring the occurrence of irreversible termination reactions, leading therefore to a loss of control.

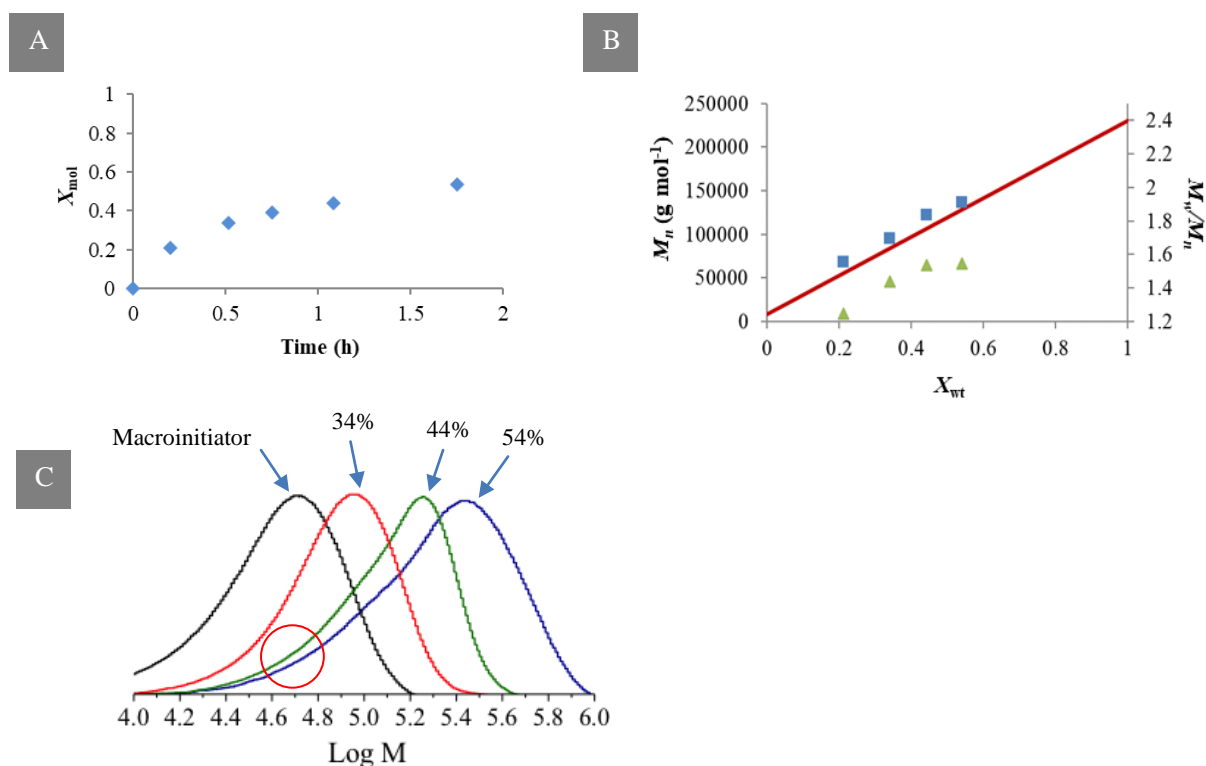




**Figure 4.** Copolymerization of MAA with MMA in the presence of 10 mol% 4VP mediated by BlocBuilder<sup>®</sup> and 15 mol% of free SG1 (based on initiator) in DMSO at 80 °C.  $M_n$  (■),  $M_w/M_n$  (▲) (determined by SEC in DMF, PMMA calibration) and size exclusion chromatograms vs weight conversion for different MMA/MAA molar ratios. A) MAA/MMA = 1/9 (MV04), B) MAA/MMA = 1/1 (MV05) and C) MAA/MMA = 3/1 (MV06). The red straight line in the  $M_n$  vs  $X_{wt}$  plot corresponds to the theoretical evolution. See Table 1 for experimental details.

### Chain extension of the P(MMA-co-4VP)-SG1 macroalkoxyamine in DMSO

To assess the living character of the 4VP-functionalized polymers, the effectiveness of the P(MMA<sub>72</sub>-co-4VP<sub>10</sub>)-SG1 macroalkoxyamine to reinitiate the NMP of BMA with a small percentage of 4VP (10 mol%) was first tested in solution. Considering the viscosity of the system, the reaction was stopped after 1.75 h as shown in Figure 5A.



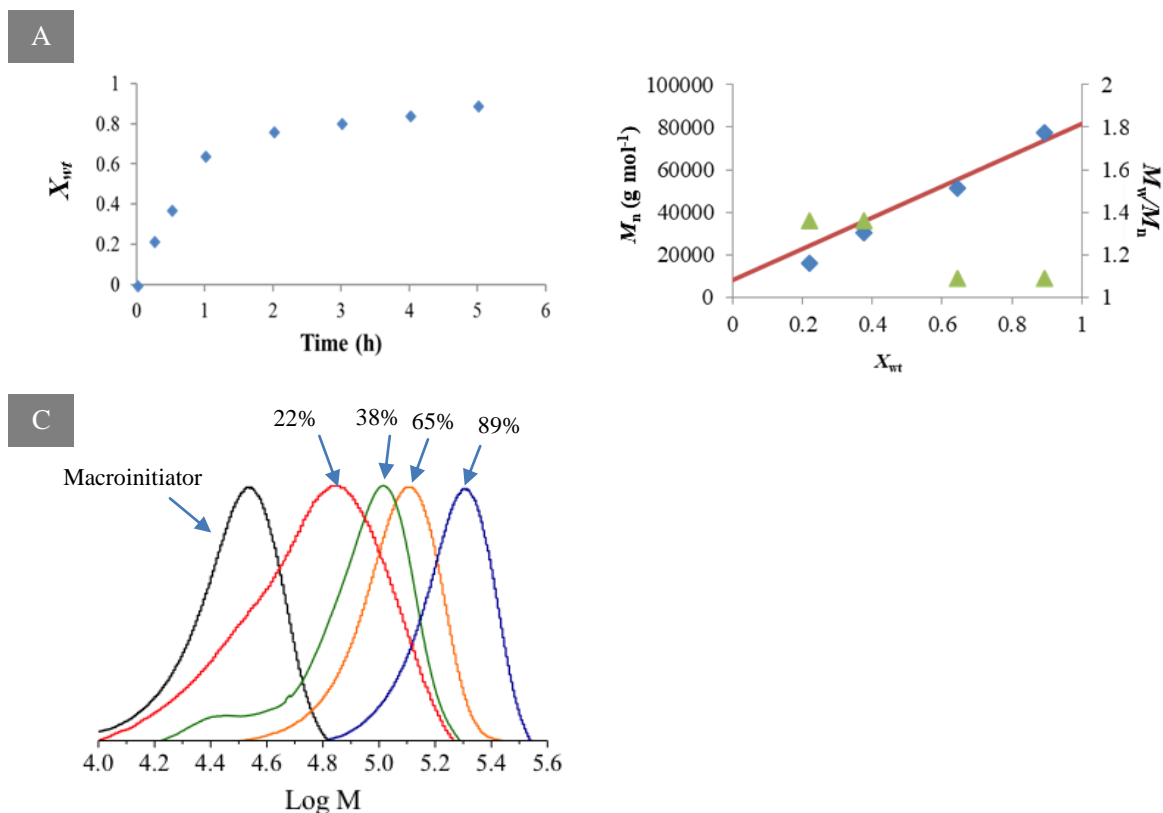
**Figure 5.** Chain extension of P(MMA<sub>72</sub>-co-4VP<sub>10</sub>)-SG1 macroinitiator with a mixture of BMA and 4VP at 85 °C in DMSO. A) Overall monomer molar conversion ( $X_{mol}$ ) vs time and B)  $M_n$  (■),  $M_w/M_n$  (▲) (determined by SEC in THF, PMMA calibration) and C) size exclusion chromatograms vs weight conversion. The red straight line in the  $M_n$  vs  $X_{wt}$  plot corresponds to the theoretical evolution.

Despite the linear increase of  $M_n$  as a function of the monomer weight conversion and the good agreement between the experimental and theoretical values (Figure 5B), the polymerization obviously exhibited a moderate level of control as attested by the high molar

mass distributions, which increased up to 1.6 with increasing conversion. As seen in Figure 5C, the SEC peaks effectively shifted with conversion but a tailing on the low molar side of the chromatograms (indicated by a red circle) was clearly visible for all the obtained copolymers. These results thus indicate the occurrence of irreversible termination reactions with the formation of dead chains either during macroalkoxyamine synthesis or during chain extension. Similar results were reported for bulk polymerization of PEGMA<sub>300</sub> and St at 80 °C initiated by BlocBuilder<sup>®</sup>, and were ascribed to the high viscosity of the reaction medium.<sup>33</sup>

***Chain extension in hydro-alcoholic medium through dispersion polymerization in the absence and in the presence of silica nanoparticles***

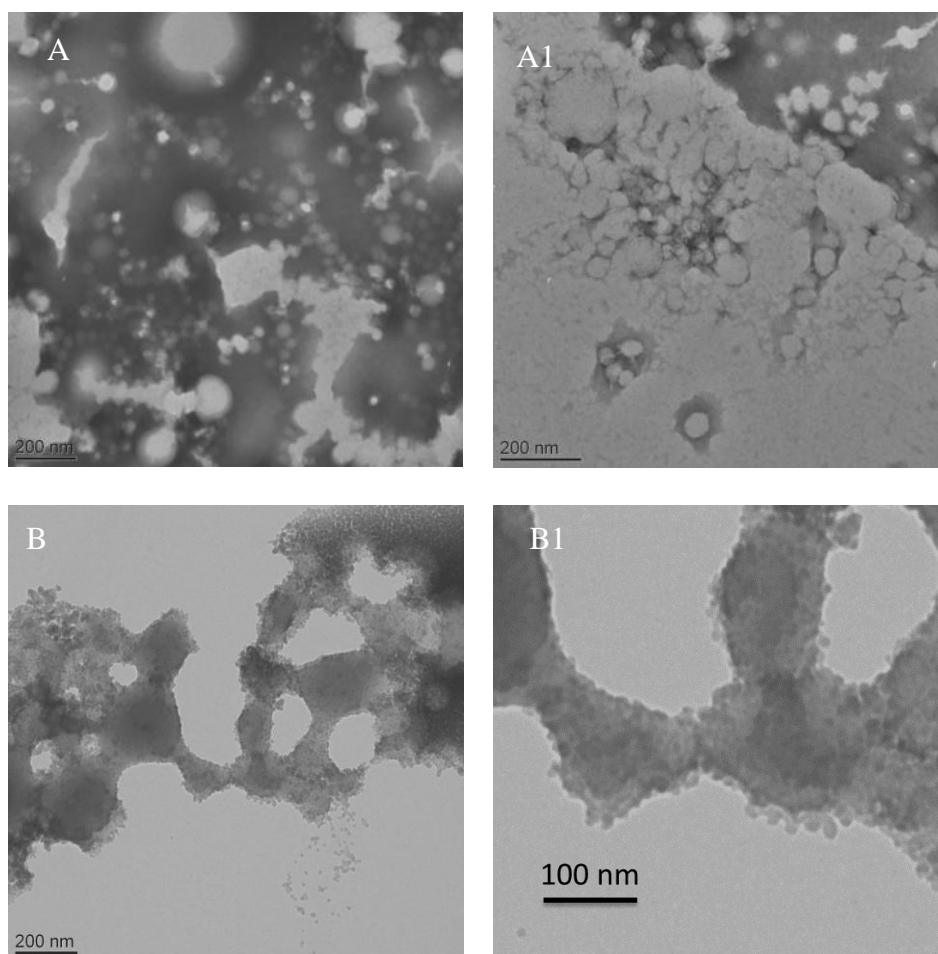
With the purpose of synthesizing polymer latex particles, the P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 macroalkoxyamine was further chain extended in an EtOH/H<sub>2</sub>O mixture (1/9 v/v) under dispersion polymerization conditions. The macroalkoxyamine initiator (2.8 mmol L<sup>-1</sup>) and the monomers (BMA and 4VP, 25.5 wt% based on total mixture) were initially soluble in this medium (the pH of the hydro-alcoholic solution was fixed at 2), while the hydrophobic P(BMA-co-4VP) block was insoluble giving rise to self-assembled block copolymers. As shown in Figure 6, the evolution of  $M_n$  (measured by SEC in DMF) as a function of the overall weight conversion (Figure 6B) shows a linear increase indicating a good control of the polymerization. In addition, the reinitiation step was quite efficient as indicated by the progressive disappearance of the peak corresponding to unreacted macroinitiator with increasing conversion (Figure 6C). The dispersity values also continuously decreased to reach values as low as 1.2 at the end of the polymerization indicating that there were less irreversible termination reactions occurring during chain extension in this case.



**Figure 6.** Dispersion copolymerization of BMA and 4VP (monomer content = 25.5 wt% and initial molar fraction of 4VP in the feed = 0.1) in hydro-alcoholic medium (EtOH/H<sub>2</sub>O: 1/9 v/v) at 85 °C using P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 as macroinitiator (2.8 mmol L<sup>-1</sup>). A) Overall monomer weight conversion ( $X_{wt}$ ) vs time and B, C)  $M_n$  (■),  $M_w/M_n$  (▲) (determined by SEC in DMF, PMMA calibration) and size exclusion chromatograms vs weight conversion. The red straight line in the  $M_n$  vs  $X_{wt}$  plot corresponds to the theoretical evolution.

DLS showed the formation of polymer particles around 314 nm in diameter with a high PDI value of 0.29. Further analysis of the latex by TEM however indicated that the particles were significantly smaller and quite polydisperse (see Figures 7A and 7A1). The discrepancy between the TEM and DLS diameters thus suggests only a moderate latex stability at the end of the polymerization despite the fact that the macroinitiator was positively charged at pH 2. It is also possible that the conditions used to measure the particle size by DLS (*i.e.*, dilution in deionized water, pH ~ 6) were not optimal to maintain the particle stability. Indeed,

unstable latexes were obtained when the polymerization was conducted at pH values higher than 2 as the macroalkoxyamine initiator became insoluble in these conditions, and could no longer play the role of a stabilizer.



**Figure 7.** TEM images of the blank (A and A1) and composite (B and B1) latex particles synthesized by dispersion polymerization of BMA and 4VP using P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 ( $M_n = 8300 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.2$ ) as macroinitiator in the absence and in the presence of 22 nm diameter silica particles, respectively.

The polymerization was then repeated in the presence of silica nanoparticles (11 wt% based on monomers) to take advantage of the well-known affinity of vinyl pyridine-based polymers for silica surfaces, and form hybrid latex particles. Narrowly size-distributed silica particles

with a number-average diameter of 22 nm were used for this purpose (see Figure S3 in the SI). As shown in Figures 7B and 7B1, the resulting polymer latex particles were fully covered by the tiny silica nanoparticles, indicating an effective interaction between the 4VP-containing macroalkoxyamine and the inorganic particles resulting in the formation of composite colloids with a raspberry-like morphology. DLS indicated the formation of 267 nm diameter latex particles with a PDI value of 0.21. It is worth noting that in this case, the pH of the suspension medium before polymerization was 6.3, which according to the blank experiments performed in the absence of silica, should result in an unstable latex. The fact that we succeeded in forming a stable latex suspension despite the high pH value of the silica dispersion, suggests that latex stabilization was ensured in this case by the tiny silica particles, that formed complexes with the 4VP units of the self-assembled copolymers, and ended-up at the latex particles surface as shown by TEM.

## CONCLUSIONS

In this work, 4VP was used as comonomer to control the NMP of methacrylic monomers under mild conditions. While the polymerization exhibited all the features of a controlled system in the case of MMA and PEOMA<sub>950</sub>, the polymerization of MAA was uncontrolled in the same conditions. 4VP was also not capable to control the copolymerization of MAA with MMA for a too large MAA content resulting in limiting conversions and broad molar mass distributions. The loss of control was tentatively ascribed to hydrogen bonding between MAA and the pyridine group of 4VP, which would influence the NMP equilibrium, and disrupt the control and livingness of the polymerization. The living character of the P(MMA<sub>72-co</sub>-4VP<sub>10</sub>)-SG1 macroalkoxyamine initiator was further assessed by chain extension experiments in both solution and dispersion polymerization, indicating the successful formation of block copolymers. At last, raspberry-like polymer/silica composite particles

were formed through dispersion NMP of BMA and a small amount of 4VP in the presence of silica nanoparticles, according to the well-known acid-base interaction between the 4VP units and the silica surface.

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