## Water-Soluble/Dispersible Carbazole-Containing

# Random and Block Copolymers by Nitroxide Mediated

**Radical Polymerization** 

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#### ABSTRACT

A series of carbazole-containing water-dispersible poly(acrylic acid-b-9-(4-vinylbenzyl)-9Hcarbazole) block copolymers (poly(AA)-b-poly(VBK)) and water-soluble poly(methacrylic acidran-9-(4-vinylbenzyl)-9H-carbazole) (poly(MAA-ran-VBK)) random copolymers were synthesized in a controlled manner (i.e low polydispersities  $(\overline{M_w}/\overline{M_n} < 1.3)$  by nitroxide mediated polymerization (NMP) using an SG1-based alkoxyamine initiator, BlocBuilder. Poly(AA)-b-poly(VBK) were most easily accessed by using poly(AA) in its protected form as the macroinitiator for the VBK block. Controlled polymerization of MAA was accomplished using an excess of 10 mol% SG1 relative to BlocBuilder with VBK as controlling co-monomer (initial molar feed content  $f_{VBK,0} = 0.03-0.79$ ) in dimethylformamide (DMF) at 80°C. Poly(MAA-ran-VBK) copolymers with a final VBK molar composition of  $F_{VBK} < 0.30$  resulted in water-soluble copolymers. In addition, the resulting poly(MAA-ran-VBK) macroinitiators were sufficiently "pseudo"-living to reinitiate a second batch of monomer (90 mol% methyl methacrylate (MMA) with styrene (S)) in organic solvent and by ab initio, surfactant-free emulsion polymerization. In both cases, low polydispersity amphiphilic block copolymers resulted ( $\overline{M_w}/\overline{M_n} < 1.3$ ).

#### **KEYWORDS**

Nitroxide mediated polymerization (NMP), 9-(4-vinylbenzyl)-9H-carbazole (VBK), watersolubility, amphiphilic copolymers, methacrylic/acrylic acid.

#### INTRODUCTION

Copolymers containing carbazole units are excellent hole transporters and electroluminescent materials that makes them viable candidates for organic-based sensors, (Ates, Sarac et al. 2009; Tam, Mak et al. 2009) organic light emitting diode materials, (Lee, Yeh et al. 2008; Yeh, Lee et al. 2008) and organic photovoltaic devices.(Grazulevicius, Strohriegl et al. 2003; Evanoff, Carroll et al. 2008) Random or statistical copolymerization is one of the easiest and most straightforward techniques of incorporating multiple functionalities such as carbazole into a polymer. For example, amphiphilic statistical copolymers containing poly(vinyl carbazole) were used to disperse CdTe nanocrystals, resulting in processible luminescent composites.(Sun, Zhang et al. 2006) The inclusion of hydrophilic comonomers has also been used to synthesize carbazole-containing amphiphilic copolymers for drug delivery with fluorescent tracing capability.(Liu, Wu et al. 2008) In other cases, amphiphilic block copolymers are known to selfassemble in aqueous solutions, resulting in nano-sized objects such as micelles and rods. Eisenberg and coworkers have examined extensively the morphology of amphiphilic block copolymers dispersed in aqueous solutions.(Zhang and Eisenberg 1998; Liu and Eisenberg 2003; Choucair, LimSoo et al. 2005) However, to maximize the benefit of self-assembly of block copolymers, the control of the molecular weight distribution along with final block composition is crucial.(Zhang and Eisenberg 1995) Since the early 1990s, the use of controlled radical polymerization (CRP) has risen exponentially as a robust, versatile and relatively simple technique to obtain such block copolymers. Among CRP techniques, the most commonly used to synthesize functional materials with controlled architectures are atom transfer radical polymerization (ATRP)(Pintauer and Matyjaszewski 2008), reversible addition fragmentation

transfer polymerization (RAFT)(Moad, Rizzardo et al. 2006; Moad, Rizzardo et al. 2009) and nitroxide mediated polymerization (NMP)(Hawker, Bosman et al. 2001; Studer and Schulte 2005; Grubbs 2011). While RAFT and ATRP are generally viewed as more versatile techniques capable of polymerizing a much wider range of monomers, NMP has some notable advantages. For example, NMP is a relatively simple polymerization technique, often only requiring a single unimolecular initiator/mediator and rarely requires post-polymerization steps such as catalyst removal.(Grubbs 2011) In addition, NMP does not rely on sulfur-based chain transfer agents like RAFT does or metallic ligands like ATRP does, which may contaminate polymers in a detrimental way for biological materials or sensitive electronic devices.(Grubbs 2011) Traditionally, NMP's major downfall, when using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) based initiators, was its ability to polymerize only styrenic monomers in a controlled manner. (Georges, Veregin et al. 1993; Veregin, Georges et al. 1993; Zetterlund, Kagawa et al. 2008) The discovery of second-generation initiators based on 2,2,5-trimethyl-4-phenyl-3azahexane-N-oxyl (TIPNO)(Benoit, Chaplinski et al. 1999) and [tert-butyl]1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino] nitroxide (DEPN or SG1)(Grimaldi, Finet et al. 2000) has allowed the homopolymerization of acrylates(Lessard, Graffe et al. 2007; Lessard and Maric 2008c; Lessard and Maric 2008a) and acrylamides(Hawker, Bosman et al. 2001). The homopolymerization of methacrylates by NMP is still problematic but methods have been developed to overcome these. Currently, commercially available initiators based on TIPNO or SG1 are unable to homopolymerize methacrylates in a controlled fashion. Grubbs and coworkers have recently developed a new N-phenylalkoxyamine based on the 4-nitrophenyl 2methylpropionat-2-yl radicals which was capable of synthesizing poly(methyl methacrylate) (poly(MMA)) homopolymers with narrow molecular weight distributions  $(\overline{M_w}/\overline{M_n} < 1.3)$  that

were pseudo-"living" enough to reinitiate a fresh batch of styrene with little to no irreversibly terminated chains.(Greene and Grubbs 2010) Methacrylates are particularly challenging for NMP since they possess a high equilibrium constant (K), which leads to a significant production of free radicals in the early stages of the polymerization, resulting in a high probability of irreversible termination reactions. (Charleux, Nicolas et al. 2005) In addition, a high degree of irreversible termination due to  $\beta$ -hydrogen transfer is observed if a large excess of SG1 is used in attempts to control the homopolymerization of poly(methacrylate)s (Dire, Belleney et al. 2008). Charleux and coworkers have determined that by using a small amount of comonomer with a low K, such as styrene, will reduce the average K,  $\langle K \rangle$ , and therefore permit control of the polymerization, which is manifested as a linear molecular weight versus conversion relationship and relatively narrow molecular weight distribution  $(\overline{M_w}/\overline{M_n} \le 1.4)$ .(Charleux, Nicolas et al. 2005) The use of styrene as a "controlling" comonomer has been successfully used to copolymerize MMA, (Charleux, Nicolas et al. 2005) ethyl methacrylate,(Lessard and Maric 2009) methacrylic acid, (Dire, Charleux et al. 2007) tert-butyl methacrylate, (Lessard, Tervo et al. 2010) benzyl methacrylate, (Zhang, Lessard et al. 2010) glycidyl methacrylate, (Moayeri, Lessard et al. 2011) oligo(ethylene glycol) methacrylates (Nicolas, Couvreur et al. 2008) and even glucose-functionalized methacrylates.(Ting, Min et al. 2009) Recently, comonomers other than styrene have emerged as suitable "controlling" comonomers that impart additional functionality into the copolymer. Some of these comonomers include polar acrylonitrile(Nicolas, Brusseau et al. 2010), water-soluble 4-styrene sulfonate(Belleney, Magnet et al. 2010) and hole-transporting 9-(4-vinylbenzyl)-9H-carbazole (VBK).(Lessard, Ling et al. 2011) The synthesis of poly(VBK) has been successfully demonstrated using TEMPO (Zhang, Yan et al. 2008) and an SG1-based 2-([tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxy)-2initiator,

methylpropionic acid (BlocBuilder).(Lessard, Ling et al. 2011) VBK is of particular interest because of its pendent carbazole unit that can impart hole transport properties into the poly(methacrylate) resin.(Grazulevicius, Strohriegl et al. 2003) We recently reported the controlled synthesis of poly(methyl methacrylate) (MMA) using VBK as the controlling comonomer with as little as 1 mol% of VBK relative to MMA with BlocBuilder.(Lessard, Ling et al. 2011) Recently, BlocBuilder as initiator and VBK as the comonomer enabled control via NMP of poly((dimethylamino) ethyl methacrylate-*ran*-9-(4-vinylbenzyl)-9H-carbazole)-*b*poly(*N*,*N* dimethyl acrylamide) thermo/pH-responsive fluorescent micelles.(Lessard and Marić 2011)

In this study, we aimed to produce, via NMP, water-soluble carbazole-containing block and random copolymers using acrylic acid (AA) or methacrylic acid (MAA) (in their neat or protected form) to impart water-solubility/dispersibility. Amphiphilic poly(AA)-*b*-poly(VBK) block copolymers were targeted by using poly(AA) macroinitiators to initiate the polymerization of VBK (**Scheme 1a**) and **b**)). Since AA homopolymerization by NMP has been known to result in a large fraction of irreversibly terminated chains due to degradation of the alkoxyamine initiator by the acid (Lessard and Maric 2008) and thus the protected form of poly(AA), such as poly(*tert*-butyl acrylate) (poly(TBA)) was used as the macroinitiator(Lessard and Maric 2008b) (**Scheme 1c**) and **d**)). The poly(*tert*-butyl acrylate)-*b*-poly(VBK) could then easily be converted to poly(AA)-*b*-poly(VBK) block copolymers by mild acid treatment (**Scheme 1e**)). Alternatively, random copolymers comprising MAA-rich compositions with VBK as the controlling comonomer (poly(MAA-*ran*-VBK)) were also synthesized and their water-solubility was evaluated as a function of VBK composition (**Scheme 1f**)). Finally, the water-soluble poly(MAA-*ran*-VBK) macroinitiators were used to initiate the polymerization of MMA/styrene (S) mixtures in organic solvent and by *ab initio* surfactant-free emulsion polymerization. In summary, these polymerizations will showcase the versatility of BlocBuilder-mediated NMP to produce water-soluble hole-transporting copolymers, which can be used in sensor applications, for example.

#### **RESULTS AND DISCUSSION**

Stabilizing carbazole-containing polymers in water was explored by first dispersing block copolymers comprised of a hydrophilic poly(AA) segment and a hydrophobic poly(9-(4-vinylbenzyl)-9H-carbazole) (poly(VBK)). As previously mentioned, the poly(AA)-*b*-poly(VBK) block copolymers were synthesized by either a VBK chain extension of poly(AA) macroinitiators (Scheme 1 a) and b)) or by a VBK chain extension of poly(TBA) macroinitiator resulting in a poly(TBA)-*b*-poly(VBK) block copolymers, which was treated with a mild acid to convert the poly(TBA)-*b*-poly(VBK) to poly(AA)-*b*-poly(VBK) (Scheme 1 c), d) and e)). The formulations for the VBK chain extensions from poly(AA) and poly(TBA) macroinitiators is summarized in Table 1. Later, MAA/VBK random copolymerizations were examined as alternative method towards water-soluble carbazole containing copolymers and the formulations are found in Table 2. The molecular characteristics of the final poly(AA)-*b*-poly(VBK) block copolymers and MAA/VBK statistical copolymers can be found in Table 3 and Table 4, respectively.

### Poly(acrylic acid)-*b*-Poly(9-(4-Vinylbenzyl)-9H-carbazole) and Poly(*tert*-butyl acrylate)-*b*-Poly(9-(4-Vinylbenzyl)-9H-Carbazole) Block Copolymer Characterization.

Both poly(AA) and poly(TBA) homopolymers were used as macroinitiators to polymerize a fresh batch of 9-(4-vinylbenzyl)-9H-carbazole (VBK). Figure 1 and Figure 2 are the GPC chromatograms of the chain extensions of a fresh batch of VBK from poly(AA) and poly(TBA) macroinitiators, respectively. In all cases, it is evident by the shift in the GPC chromatograms that all the macroinitiators used in this study were sufficiently pseudo-"living" to re-initiate a second batch of monomer, but it is also clear that some poly(AA) chains were not re-initiated. The molecular weight characteristics of the macroinitiators along with the final block copolymers are found in Table 4. After the VBK chain extensions, the poly(AA) macroinitiators experienced an increase in  $\overline{M_n}$  from 5.4 - 8.4 to 13.3 - 13.6 kg·mol<sup>-1</sup> with a slight broadening of the  $\overline{M_w}/\overline{M_n}$  from 1.21 - 1.24 to 1.56 - 1.65. The poly(TBA) macroinitiators experienced similar increases in  $\overline{M_n}$  from 4.6 - 21.5 to 17.3 - 22.0 kg·mol<sup>-1</sup> while experiencing less noticeable increases in  $\overline{M_w}/\overline{M_n}$  from 1.23 - 1.29 to 1.26 - 1.39. However, as indicated by the increase in  $\overline{M_w}/\overline{M_n}$  and the slight inflection on the right side of the molecular weight distribution in **Figure** 1, it is possible that a significant concentration of the poly(AA) macroinitiators were irreversibly terminated and were therefore still present in the final sample. In the case of the poly(TBA) macroinitiators, no apparent inflection is visible in Figure 3, indicating that the poly(TBA) macroinitiators possessed a higher degree of pseudo-"livingness" compared to the poly(AA) macroinitiators, which is agreement with previous work. SG1-capped poly(TBA) macroinitiators were found to have higher degrees of pseudo-"livingness" compared to poly(AA) macroinitiators for the chain extension with styrene.(Lessard and Maric 2008b) The addition of VBK to the block copolymers was also monitored by <sup>1</sup>H NMR spectroscopy. As indicated in **Table 4**, for the poly(TBA)-*b*-poly(VBK) block copolymers, the mole fraction of VBK in the copolymer,  $F_{VBK}$ , ranges from 0.27 to 0.51 while in the case of poly(AA)-*b*-poly(VBK) block copolymers, the  $F_{VBK}$  ranges from 0.26 to 0.48. The  $F_{VBK}$  of the poly(AA)-*b*-poly(VBK) block copolymers may actually be somewhat lower due to the presence of irreversibly terminated poly(AA) homopolymers, since the secondary peak corresponding to the poly(AA) macroinitiator in the GPC could not be reduced or removed, even after multiple washings and fractionations. The same problem was not evident for the poly(TBA)-*b*-poly(VBK) block copolymers. In summary, BlocBuilder was capable of synthesizing poly(AA)-*b*-poly(VBK) and poly(TBA)-*b*-poly(VBK) block copolymers with relatively similar  $\overline{M_n}$  and copolymer compositions. Poly(TBA) was however more effective as a macroinitiator due to the lack of free acid groups that poly(AA) possess, which degrade the alkoxyamine and thus lead to seemingly broader molecular weight distributions. Thus, access to poly(AA)-*b*-poly(VBK) block copolymers by NMP is best done be using poly(AA) in its protected form.

The poly(AA)-*b*-poly(VBK) block copolymers converted from poly(TBA)-*b*-poly(VBK) were dispersed in water according to the literature (Zhang and Eisenberg 1998; Zhang and Eisenberg 1999)(see characterization section for details on deprotection and solubility). The poly(AA)-*b*-poly(VBK) synthesized directly from poly(AA) macroinitiators were not used because of the presence of poly(AA) homopolymers present from the polymerization, as indicated in the GPC chromatograms. While the block copolymers could easily be dispersed in aqueous solution as micelle-like aggregates, they did not remain suspended in solution, resulting in significant precipitation over approximately 2 days. The particle diameter was measured by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Using either

method, a broad distribution of agglomerate sizes between 0.2 to 2.5  $\mu$ m was observed. In contrast to water-dispersible aggregates, we next focused on alternative strategies to make carbazole-functional copolymers that were entirely soluble in aqueous media.

#### Methacrylic acid (MAA)/9-(4-Vinylbenzyl)-9H-Carbazole (VBK) Copolymerizations using BlocBuilder

While the polymerization of acrylates is feasible by BlocBuilder-mediated NMP, the presence of intramolecular chain transfer reactions such as "back biting" are high and are known to affect the molecular architecture of the final polymer due to the formation of mid-chain radical structures (i.e. long chain branching).(Arzamendi, Plessis et al. 2003; Asua, Beuermann et al. 2004) Methacrylates do not undergo such reactions and thus result in a more linear final polymer. As mentioned in the introduction, the homopolymerization of methacrylates by BlocBuilder results in poor polymerization control. However, the addition of a small fraction of "controlling" comonomer such as styrene or VBK in the feed can result in a controlled copolymerization. The use of VBK as a "controlling" comonomer for MAA was therefore investigated. In this study, various copolymers were synthesized at 80 °C in a 20 wt% DMF solution using different initial molar feed fractions of VBK ( $f_{VBK,0}$ ). The experimental formulations along with the molecular weight characterization of the final copolymers can be found in Table 1 and Table 3, respectively. MAA/VBK-1 was done in 1,4-dioxane and while heating the mixture, it was noticed that a significant portion of VBK did not start becoming soluble until approximately a temperature of 65°C was reached. At this point, MAA had already started polymerizing and the mixture had become extremely viscous before even reaching 75 °C. When using DMF, both VBK and MAA were soluble at low temperatures and the copolymerization therefore took place

in a controlled manner. Figure 3a) shows the progression of  $\ln((1-X)^{-1})$  (X = conversion) versus time and Figure 3b) shows the growth of  $\overline{M_n}$  and  $\overline{M_w}/\overline{M_n}$  with respect to X for the characteristic copolymerization of MAA with VBK (MAA/VBK-20,  $f_{VBK,0} = 0.20$ ). The growth of  $\overline{M_n}$  versus X appeared to be linear. However, it does not follow the expected theoretical  $\overline{M_n}$ versus X. This discrepancy between the theoretical and experimentally obtained  $\overline{M_n}$  values could be due to irreversible termination of the oligomers as a result from the unprotected acid group degrading the SG1.(Lessard, Schmidt et al. 2008) Nevertheless, the samples drawn during the copolymerization still exhibited relatively narrow and monomodal molecular weight distributions ( $\overline{M_w}/\overline{M_n} \le 1.3$ ) as seen in the GPC chromatogram (Figure 3c)). The MAA/VBK copolymerizations were purposely kept to low X to maximize the pseudo-"livingness" and some were also synthesized to be water-soluble (by minimizing the hydrophobic VBK content in the feed) so that the final copolymers could be used as effective water-soluble macroinitiators. In all cases, the MAA/VBK final molar copolymer composition with respect to VBK ( $F_{VBK}$ ) was higher than the corresponding  $f_{VBK,0}$  (Table 3, Figure 4a)). This is consistent with MMA/VBK copolymerizations and suggests a preferential VBK reactivity towards adding to itself. (Lessard, Ling et al. 2011) A series of poly(MAA-ran-VBK) copolymers were synthesized (Table 3) with  $0.04 < F_{VBK} < 0.99$  to determine the solubility limit in aqueous solution. Figure 4b) depicts the effect of copolymer composition and  $\overline{M_n}$  on final copolymer water-solubility. It was found that  $F_{VBK} < 0.3$  in the final copolymer was required for water-solubility.

### Determination of Poly(MAA-*ran*-VBK) Copolymer Pseudo-"Livingness" by Chain Extension.

Homopolymer or copolymer degree of pseudo-"livingness" was characterized by the ability to reinitiate a fresh batch of monomer. Other methods have been developed to determine the fraction of living chains, such as using a fluorescent tracer(Cunningham, Lin et al. 2005), <sup>31</sup>P NMR spectroscopy (since phosphorus is present in SG1)(Nicolas, Dire et al. 2006) and electron spin resonance (ESR).(Nicolas, Dire et al. 2006) Chain extensions are straightforward, can give insightful results and are therefore most often used to determine the chain pseudo-"livingness".(Lessard and Maric 2008b; Lessard, Ling et al. 2011) Chain extensions of VBK from various poly(MAA-ran-VBK) macroinitiators were performed to determine their pseudo-"livingness" (Table 2). The molecular characterization of all chain extensions can be found in Table 4. MAA/VBK-3 was used as a characteristic copolymer macroinitiator, because it was still water-soluble but contained a relatively high concentration of VBK in the final copolymer. The shifts in the GPC chromatograms of the chain extensions shown in Figure 5 clearly show the shift in elution time demonstrating the increase in  $\overline{M_n}$  with time. Figure 5a) shows the shift in GPC traces from the MAA/VBK-3 macroinitiator to the final MAA/VBK-3-VBK block copolymer. The MAA/VBK-3 macroinitiator experienced an increase in  $\overline{M_n}$  from 12.5 kg·mol<sup>-1</sup> to 22.2 kg·mol<sup>-1</sup> with an increase in  $\overline{M_w}/\overline{M_n}$  from 1.37 to 1.57. However, it is apparent from the GPC chromatogram for the MAA/VBK-3-VBK block copolymer that it possesses a "hump" at higher elution times, signifying a strong possibility that irreversible termination took place during the copolymerization of MAA/VBK and that some of the chains were not being reinitiated. Therefore, MAA/VBK-B was formulated to have a similar  $F_{VBK}$  as MAA/VBK-3 but was synthesized to a lower X and with a lower  $\overline{M_n}_{Target}$  to hopefully provide a higher fraction of pseudo-"living" chains compared to MAA/VBK-3. Figure 5b) shows the chain extension of MAA/VBK-B using a fresh batch of a methyl methacrylate (MMA)/styrene (S) mixture (approximately 90 mol% MMA in the second batch) to give poly(MAA-*ran*-VBK)-*b*-poly(MMA-*ran*-S). MAA/VBK-B increased its  $\overline{M_n}$  from 3.3 kg·mol<sup>-1</sup> to 46.2 kg·mol<sup>-1</sup> with nearly no change in  $\overline{M_w}/\overline{M_n}$  (1.28 before to 1.26 after chain extension). This latter experiment shows that MAA/VBK copolymers could be designed to be water-soluble and can also be used as macroinitiators for a clean chain-extension with non-polar monomers.

#### Surfactant-Free Ab Initio Emulsion Polymerization

The synthesis of amphiphilic block copolymers by controlled radical emulsion polymerization would reduce the cost of manufacturing of these materials, be more environmentally friendly (by reducing the use of organic solvents) and thus increase their industrial applicability.(Cunningham 2008; Min and Matyjaszewski 2009; Destarac 2010) The use of water as the continuous phase, apart from its obvious economic and environmental implications, can also lead to controlled polymerizations with much higher conversions than in bulk ( $\approx$ 100%).(Cunningham 2008; Oh 2008; Zetterlund, Kagawa et al. 2008) NMP has been adapted to polymerization in aqueous media via emulsion or miniemulsion polymerization.(Nicolas, Ruzette et al. 2007; Cunningham 2008; Zetterlund, Kagawa et al. 2008)Even more attractive is the possible *ab initio* surfactantfree NMP emulsion polymerization enabled by suitable water-soluble SG1-capped macroinitiators. Charleux et al. have successfully prepared amphiphilic block copolymers using nitroxide mediated emulsion polymerization by means of a previously synthesized water-soluble macroinitiator of poly(acrylic acid)(Delaittre and Charleux 2008) or of poly(methacrylic acid*ran*-styrene)(Dire, Magnet et al. 2009) to initiate a second batch of non-polar monomer in either a pressurized reactor or under ambient conditions.(Dire, Magnet et al. 2009) This technique has also been used towards the synthesis of thermosensitive nano-gels(Delaittre, Save et al. 2007) and copolymer vesicles based on 4-vinylpyridine copolymers (Delaittre, Dire et al. 2009).

The sample MAA/VBK-B was determined to be sufficiently "living" to re-initiate a fresh batch of monomers (MMA/S; ~ 90 mol% MMA in the second batch) in organic solution. MAA/VBK-B was then used as a "surfmer" or reactive surfactant, in the surfactant-free *ab initio* emulsion polymerization of MMA/S (Scheme 2). The neutralized MAA/VBK-B was solubilized in water prior to monomer addition and then reacted for 8 hours with the MMA/S mixture at 90 °C. An increase in  $\overline{M_n}$  from 3.3 kg·mol<sup>-1</sup> to 43.7 kg·mol<sup>-1</sup>, with little to no change in  $\overline{M_w}/\overline{M_n} =$ 1.28 to  $\overline{M_w}/\overline{M_n} =$  1.24, was observed. The GPC chromatogram of MAA/VBK-MMA/S-2 revealed a narrow molecular weight distribution with little to no apparent peaks due to unreacted macroinitiator (Figure 6). These results indicate that poly(MAA-*ran*-VBK) synthesized by NMP can be successfully re-initiated to polymerize an MMA/S mixture in organic solution as well as by *ab initio* emulsion polymerization, resulting in an amphiphilic block copolymer characterized by a narrow molecular weight distribution.

The use of VBK not only can act as a controlling comonomer for MAA by BlocBuildermediated NMP, resulting in low polydispersity and pseudo-"living" copolymers, but also introduces carbazole units, which are fluorescent(Lessard and Marić 2011) and have holetransport properties(Grazulevicius, Strohriegl et al. 2003). This added functionality makes such materials interesting for sensor applications in aqueous media. Future studies will be directed towards assessing similar block copolymers for such uses.

#### Conclusion

Low polydispersity poly(AA)-*b*-poly(VBK) amphiphilic block copolymers ( $\overline{M_w}/\overline{M_n} < 1.3$ ) were synthesized by VBK chain extensions using poly(TBA) macroinitiators, followed by cleaving of the *tert*-butyl protecting group, and by a direct chain extension from poly(AA). The poly(TBA) macroinitiators appeared to be significantly more pseudo-"living" than the poly(AA) macroinitiators, resulting in a much lower concentration of unreacted chains which could be separated from the block copolymer using typical fractionation methods. However, when using the poly(AA) macroinitiators, the presence of "dead" chains was significant, which could not be removed by fractionation from the final block copolymers. A characteristic poly(TBA)-*b*-poly(VBK) block copolymer which was then neutralized and dispersed in an aqueous solution and characterized by aggregates with a diameter of 0.2-2.3 µm, measured by DLS and TEM. However, the colloidal stability was low as the final block copolymer began settling out of solution almost immediately.

In the second part of the study, VBK was used as a "controlling" comonomer for the pseudo-"living" statistical copolymerization of MAA resulting in a linear increase in  $\overline{M_n}$  versus X (up to X = 0.4) and a final copolymer with narrow molecular weight distribution ( $\overline{M_w}/\overline{M_n} < 1.3$ ). Copolymers were made with various VBK content ( $F_{VBK} = 0.1 - 0.99$ ) and were comparatively richer compared to the respective feed composition. In addition to controlling the copolymerization, VBK introduced carbazole units, which are known to be fluorescent and have hole-transport properties, into the final copolymer while maintaining the water-solubility, provided the copolymer composition was not too high in VBK ( $F_{VBK} < 0.3$ ). The final copolymers were determined to be pseudo-"living" after subsequent chain extensions in organic

solution as well as by surfactant-free *ab initio* emulsion polymerization resulting, in both cases, in a well-defined amphiphilic block copolymer ( $\overline{M_w}/\overline{M_n} < 1.3$ ).

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#### EXPERIMENTAL SECTION

#### Materials

Methacrylic acid (MAA, 99%), methyl methacrylate (MMA, 95%), styrene (S, 99%) anhydrous diethyl ether (> 99%), sodium hydroxide (NaOH), basic alumina (Brockmann, Type 1, 150 mesh), calcium hydride (90–95%, reagent grade) were obtained from Aldrich. Prior to use, the MMA and styrene were purified by passage through a basic alumina/calcium hydride (40 to 1 volume ratio) column and stored under a head of nitrogen in a freezer until required. Methanol (99.8%), tetrahydrofuran (THF, 99.5%), 1,4 dioxane (99.5%), *N*,*N*-dimethylformamide (DMF, 99.5%) and HPLC grade DMF (99.9%) were all obtained from Fisher Scientific Canada. Deuterated chloroform (CDCl<sub>3</sub>, 99.8%) was obtained from Cambridge Isotopes Laboratories. 2-

([*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxy)-2-methylpropionic acid (BlocBuilder<sup>TM</sup>, 99%) was obtained from Arkema and [*tert*-butyl[1-(diethoxyphosphoryl)-2,2dimethylpropyl]amino] nitroxide (SG1, 85%) was kindly donated by Noah Macy of Arkema and both were used as received. 9-(4-vinylbenzyl)-9H-carbazole (VBK) was synthesized according to the literature.(Cho, Kim et al. 2001; Zhang, Yan et al. 2008) Poly(acrylic acid) (poly(AA)) and poly(tert-butyl acrylate) (poly(TBA)) macroinitiators were also synthesized according to the literature.(Lessard, Graffe et al. 2007; Lessard, Tervo et al. 2009)

### Chain extension of 9-(4-vinylbenzyl)-9H-carbazole (VBK) from either poly(*tert*-butyl acrylate) (poly(AA)) or poly(acrylic acid) (poly(TBA)) macroinitiators

The synthetic procedure for poly(acrylic acid) and poly(*tert*-butyl acrylate) macroinitiators has previously been reported.(Lessard, Graffe et al. 2007; Lessard, Schmidt et al. 2008) The chain extensions were performed in a 3-neck, 50 ml round bottom glass reactor outfitted with a condenser, which was cooled with 50wt% ethylene glycol to water mixture circulated using a Neslab chiller. The temperature was measured by a thermocouple, which was inserted into a thermowell in the reactor and connected to a temperature controller and heating mantel on which the reactor was mounted. The third opening of the reactor was sealed with rubber septa, allowing for easy sampling by syringe. All formulations for VBK chain extensions from PAA and TBA macroinitiators are shown in **Table 2**. The synthesis procedure of TBA-VBK-2 is given as an example. To the reactor was added the previously synthesized poly(TBA) macroinitiator (TBA-2, 0.25 g,  $\overline{M_n} = 10.1$  kg mol<sup>-1</sup>,  $\overline{M_w}/\overline{M_n} = 1.23$ ), VBK (1.38 g, 5.1 mmol) and 1,4-dioxane (13.0 g) solvent. The reactor was then heated to 105 °C while continuing with a light nitrogen purge throughout the entire reaction. The resulting solution was precipitated and washed 3 times with methanol and dried under vacuum at 60 °C to obtain the TBA-VBK-2 block copolymer, characterized by a final yield of 0.02 g (2%),  $\overline{M_n} = 17.5$  kg mol<sup>-1</sup>, and  $\overline{M_w}/\overline{M_n} = 1.39$ . All final copolymers that were found to have a bimodal molecular distribution as observed from the GPC chromatograms were fractionated from THF with methanol to remove the macroinitiators that failed to re-initiate. The low yield is a result from the losses due to fractionation.

Synthesis of Methacrylic Acid (MAA)/9-(4-Vinylbenzyl)-9H-Carbazole (VBK) Copolymers MAA/VBK copolymerizations were done in a similar setup and fashion to the VBK chain extensions. For example, for the synthesis of MAA/VBK-20, BlocBuilder (32.6 mg, 0.085 mmol), free SG1 (2.7 mg, 0.0092 mmol), MAA (1.29 g, 14.9 mmol), VBK (1.01 g, 3.7 mmol) and DMF (9.8 g  $\approx$  20 wt% solution) were added to the reactor prior to purging and sealing. All MAA/VBK reactions were performed at 80 °C and all formulations were calculated to have a target molecular weight at complete conversion of  $\overline{M_n} \approx 21 \text{ kg} \cdot \text{mol}^{-1}$ ; formulations can be found in **Table 1**. Samples as well as the final copolymer were precipitated in diethyl ether. The crude product was washed with methanol and dried overnight in a vacuum oven at 60 °C resulting in a white powder. All samples were then methylated using trimethylsilyldiazomethane prior to GPC analysis (see characterization section). In this example, the final random copolymer was characterized by X = 0.24,  $\overline{M_n} = 5.5 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.16$ ,  $F_{VBK} = 0.36$ .

### Synthesis of Poly(Methacrylic acid-*ran*-9-(4-Vinylbenzyl)-9H-Carbazole)-*b*-poly(Methyl Methacrylate-*ran*-Styrene) (poly(MAA-*ran*-VBK)-*b*-poly(MMA-*ran*-S))

All chain extensions, regardless of the macroinitiator used, were done in an identical setup to the MAA/VBK copolymerizations. As an example, MAA/VBK-B (0.11 g, 0.033 mmol), MMA (7.75 g, 77.5 mmol), styrene (0.86 g, 8.26 mmol) and DMF (5.6 g) were added to the reactor and sealed. Once the solution was bubbled, the reactor temperature was set (90 °C in this example) and the reaction was allowed to proceed under light nitrogen purge for 150 minutes. Once the reaction was complete, the solution was cooled and the product was precipitated from methanol. All samples were then methylated using trimethylsilyldiazomethane prior to GPC analysis (see characterization section). The product was recovered and characterized (yield = 0.1 g,  $\overline{M_n}$  = 46.2 kg·mol<sup>-1</sup>,  $\overline{M_w}/\overline{M_n}$  = 1.26,  $F_{VBK} < 0.01$  and  $F_{styrene}$  = 0.20).

# Synthesis of Poly(Methacrylic Acid-*ran*-9-(4-Vinylbenzyl)-9H-Carbazole)-*b*-poly(Methyl Methacrylate-*ran*-Styrene) (poly(MAA-*ran*-VBK)-poly(MMA-*ran*-S)) Block Copolymers by Surfactant Free *ab-initio* Polymerization

In a similar reactor set-up to all the chain extensions, MAA/VBK-B (0.11 g, 0.033 mmol) was solubilized in a dilute aqueous NaOH solution (10.1 g water, 57.3 mg of NaOH (1.43 mmol) and 67.2 mg of Na<sub>2</sub>CO<sub>3</sub> (0.63 mmol) to neutralize the macroinitiator and bring the pH = 10). Once the macroinitiator was solubilized, MMA (2.52 g, 25.2 mmol) and S (0.26 g, 2.49 mmol) were added to the reactor followed by vigorous agitation and nitrogen bubbling for 20 minutes. The biphasic mixture was then heated to 90 °C and allowed to react for 5 hours. The emulsion had a milky consistency and appeared to be stable throughout the reaction. Samples as well as the final copolymer were acidified with HCl and dried by rotary evaporation. The acidified block

copolymers were solubilized in 1,4-dioxane and filtered using 0.2µm Teflon filters (NaCl, a product of the acidification, was separated from the solution). The crude product was dried over night in a vacuum oven at 60 °C. All samples were then methylated using trimethylsilyldiazomethane prior to GPC analysis (see characterization section). The final block copolymer was characterized by GPC and NMR ( $\overline{M_n} = 43.7 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.24$ ,  $F_{\text{VBK}} < 0.01$  and  $F_{\text{styrene}} = 0.20$ ).

#### Characterization

Conversion of the poly(MAA-*ran*-VBK) copolymerizations was determined by gravimetry. Prior to gravimetric analysis, the samples were washed 2-3 times using MeOH to remove the unreacted VBK monomer. <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> was used to determine if the VBK monomer was completely removed from the samples. All <sup>1</sup>H NMR spectroscopy measurements were done with a 300 MHz Varian Gemini 3000 spectrometer using 5 mm Up NMR tubes. Molecular weight characterization was determined using gel permeation chromatography (GPC, Waters Breeze). The GPC was equipped with both ultra-violet (UV 2487) and differential refractive index (RI 2410) detectors. The methacrylic acid and acrylic acid containing statistical copolymers and block copolymers were reacted with trimethylsilyldiazomethane (2.0 M in hexanes), to convert the acid groups into methyl esters, prior to injection into the GPC, in order to methylate the acidic monomer units, and thereby eliminate possible column interactions.(Couvreur, Lefay et al. 2003). The copolymers were characterized using 3 Waters Styragel HR columns: HR1 with molecular weight measurement range of  $10^2$  to  $5 \times 10^3$  g·mol<sup>-1</sup>, HR2 with molecular weight measurement range of  $5 \times 10^2$  to  $2 \times 10^4$  g·mol<sup>-1</sup> and HR4 with molecular weight measurement range 5 x 10<sup>3</sup> to 6 x 10<sup>5</sup> g·mol<sup>-1</sup> which were heated to 40 °C during the analysis. The molecular weights were determined by calibration with linear narrow molecular weight distribution poly(styrene) standards. Appropriate Mark-Houwink coefficients were used to convert molecular weights based on poly(styrene) ( $K_{poly(styrene)} = 11.4 \times 10^{-5} \text{ dL} \cdot \text{g}^{-1}$ and  $\alpha_{polv(styrene)} = 0.716$  (Hutchinson, Paquet et al. 1995) to the corresponding poly(MMA)  $(K_{polv(MMA)} = 9.44 \text{ x } 10^{-5} \text{ dL} \cdot \text{g}^{-1}$  and  $\alpha_{polv(MMA)} = 0.719$  (Beuermann, Buback et al. 2000) and poly(styrene) values to corresponding poly(TBA) ( $K_{polv(TBA)} = 3.3 \times 10^{-5}$  and  $\alpha_{polv(TBA)} =$ 0.80)(Mrkvickova and Danhelka 1990) and poly(methyl acrylate) (MA, for polymer with methylated acrylic acid segments) ( $K_{poly(MA)} = 9.5 \times 10^{-5} \text{ dL} \cdot \text{g}^{-1}$  and  $\alpha_{poly(MA)} = 0.719$ )(Couvreur, Piteau et al. 2001). The reader should note that no coefficients were found in the literature for the VBK-containing polymers and therefore are based on relative PS standards. The THF mobile phase flow rate was 0.3 mL·min<sup>-1</sup>. Final copolymer composition was determined by <sup>1</sup>H NMR spectroscopy of the methylated samples using the characteristic resonances in CDCl<sub>3</sub>. The composition of poly(MAA-ran-VBK) copolymers was determined by comparing the resonances associated to the MMA (O-CH<sub>3</sub>,  $\delta = 3.75$  ppm) and the VBK (Ar-CH<sub>2</sub>-Ar,  $\delta = 5.64$  ppm). The composition of poly(MAA-ran-VBK)-b-(MMA/S) block copolymers was determined by comparing the resonances associated to the MMA (O-CH<sub>3</sub>,  $\delta = 3.75$  ppm), the VBK (Ar-CH<sub>2</sub>-N,  $\delta = 5.64$  ppm) and the styrene (Ar, 5H,  $\delta = 7.1-7.3$  ppm) units. The composition of poly(TBA)-bpoly(VBK) block copolymers was determined by comparing the resonances associated to the TBA (O-(CH<sub>3</sub>)<sub>3</sub>,  $\delta = 1.5$  ppm) and the VBK (Ar-CH<sub>2</sub>-N,  $\delta = 5.64$  ppm) while the composition of poly(AA)-b-poly(VBK) block copolymers was determined by comparing the resonances associated to the methyl acrylate (O-CH<sub>3</sub>),  $\delta = 3.76$  ppm) and the VBK (Ar-CH<sub>2</sub>-N,  $\delta = 5.64$ ppm). Water solubility of the MAA/VBK copolymers was determined by adding a small amount

of copolymer ( $\approx$ 10-50 mg) in a vial followed by the addition of a basic aqueous mixture (4-5 ml, using NaOH, pH  $\approx$  11). The sample was agitated and heated (30-50°C if necessary) for several minutes and allowed to rest for 24 hours. If the sample was not solubilized after several cycles of heating, agitating and resting ( $\approx$ 1-2 hours) then the sample was deemed insoluble in water.

#### Cleaving of tert-butyl group and water solubility test of block copolymers

The cleaving of the *tert*-butyl group, that is present in the poly(TBA)-*b*-poly(VBK) block copolymers, revealing the acid group (converting TBA units to AA units), was performed using a method previously reported.(Lessard and Maric 2008b; Lessard, Tervo et al. 2010) To a mixture of poly(TBA)-*b*-poly(VBK) block copolymers and dichloromethane, a 5x molar excess of trifluoroacetic acid (TFA) was added and reacted for 14 hours. The dichloromethane was stripped using a nitrogen purge and the final product was dried in a vacuum oven at 60 °C overnight. Aqueous dispersion of the poly(AA)-*b*-poly(VBK) (converted from poly(TBA)-*b*-poly(VBK)) was performed according to the literature.(Zhang and Eisenberg 1998; Zhang and Eisenberg 1999) A 2 wt% solution of block copolymer in *N*,*N*-dimethylformamide (DMF) was stirred vigorously while water was added at a rate of about 1 drop per 5 seconds until reaching a final emulsion of 25 wt% organic solution relative to water. The emulsion was dialyzed against pure water for 4 days to remove the DMF. For imaging, a drop was placed on a TEM grid for 30 seconds prior to removing the excess water with tissue. Transmission electron microscopy (TEM) was performed using a Philips CM-200 kV TEM using Carbon/Formvar coated Cu grids.

#### **Figure Captions**

**Scheme 1** – Various homopolymers, random copolymers and block copolymers synthesized by an SG1-based alkoxyamine initiator under various conditions; where (a) is the homopolymerization of acrylic acid (AA) followed by (b) the chain extension with 9-(4vinylbenzyl)-9H-carbazole (VBK); (c) is the homopolymerization of *tert*-butyl acrylate (TBA) followed by (d) the chain extension of poly(TBA) with a fresh batch of VBK which was then converted (e) from poly(TBA)-*b*-poly(VBK) to poly(AA)-*b*-poly(VBK) by cleaving the tertbutyl group using trifluoroacetic acid; and (f) is the copolymerization of methacrylic acid (MAA) and VBK. All experimental conditions can be found in **Table 1** and **Table 2** and final homopolymer/copolymer characterization can be found in **Table 3** and **Table 4**, respectively.

**Scheme 2** –Amphiphilic block copolymer synthesis routes utilizing SG1-capped macroinitiators. Reaction (a) shows the chain extension of poly(methacrylic acid-*ran*-9-(4-vinylbenzyl)-9Hcarbazole) (poly(MAA-*ran*-VBK)) with a fresh batch of methyl methacrylate / styrene (MMA/S) monomers and (b) is the *ab-initio* surfactant-free emulsion polymerization of MMA/S by the neutralized poly(MAA-*ran*-VBK). All experimental conditions and final block copolymer characterization can be found in **Table 1** and **Table 3** respectively. The green circles represent the SG1 groups, and the large purple circle represents the MMA/S swelled micelle which is stabilized by the neutralized poly(MAA-*ran*-VBK) chains.

**Figure 1**. Gel permeation chromatograms of a) experiment PAA-VBK-1 where the dashed gray line is PAA-1 ( $\overline{M_n} = 8.4 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.24$ ), the macroinitiator used to reinitiate VBK giving PAA-VBK-1, which is represented by the solid black line ( $\overline{M_n} = 13.3 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n}$  = 1.56,  $t_{polymerization}$  = 7 hours); and b) PAA-VBK-4 where the gray dashed line is PAA-4 macroinitiator ( $\overline{M_n}$  = 5.4 kg·mol<sup>-1</sup>,  $\overline{M_w}/\overline{M_n}$  = 1.21), and the solid black line is PAA-VBK-4 ( $\overline{M_n}$  = 13.6 kg·mol<sup>-1</sup>,  $\overline{M_w}/\overline{M_n}$  =1.65,  $t_{polymerization}$  = 7 hours). Chain extensions were both done in 1,4-dioxane at 100°C.

**Figure 2.** Gel permeation chromatograms of a) experiment TBA-VBK1 where the dashed gray line is TBA-1 ( $\overline{M_n} = 4.6 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.29$ ), the macroinitiator used to reinitiate VBK giving TBA-VBK-1 which is represented by the solid black line ( $\overline{M_n} = 17.3 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.35$ ,  $t_{polymerization} = 8$  hours); b) TBA-VBK-2 where the gray dashed line is TBA-2 macroinitiator ( $\overline{M_n} = 10.1 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.23$ ), and the solid black line is TBA-VBK-2 ( $\overline{M_n} = 17.5 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.39$ ,  $t_{polymerization} = 8$  hours); and c) TBA-PVBK-3 where the gray dashed line is TBA-3 macroinitiator ( $\overline{M_n} = 15.0 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.25$ ), and the solid black line is TBA-VBK-3 ( $\overline{M_n} = 21.2 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.36$ ,  $t_{polymerization} = 6$  hours). Chain extensions were done in 1,4-dioxane at 100°C and underwent fractionation from THF with methanol/H<sub>2</sub>O (50:50) to remove unreacted macroinitiator.

**Figure 3.** Synthesis of MAA/VBK-20 random copolymer (initial molar feed fraction  $f_{MAA,0} = 0.20$ , Table 1), a characteristic methacrylic acid/9-(4-vinylbenzyl)-9H-carbazole (MAA/VBK) copolymerization where a) is the semi-logarithmic plot of conversion (ln((1-X)<sup>-1</sup>) (X = conversion) versus time and b) is the number average molecular weight  $\overline{M_n}$  versus X and polydispersity index (PDI =  $\overline{M_w}/\overline{M_n}$ ) versus X and c) shows the gel permeation chromatograms

with samples taken at 80 min (dotted line, X = 0.23,  $\overline{M_n} = 4.4 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.09$ ); 150 min (dashed line, X = 0.31,  $\overline{M_n} = 5.0 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.11$ ); 283 min, (solid line, X = 0.41,  $\overline{M_n} = 5.5 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.20$ ,  $F_{VBK} = 0.36$ ) The reactions were all done in 20 wt% DMF solution at 80 °C.

**Figure 4.** Poly(MAA-*ran*-VBK) random copolymers with final VBK molar composition ( $F_{VBK}$ ) plotted versus a) initial molar feed composition used during the synthesis ( $f_{VBK,0}$ ) and b) the number average molecular weight ( $\overline{M_n}$ ) of the final copolymer. The dashed line in a) is just a visual guide and does not represent a fit to a theoretical expression relating  $F_{VBK}$  to  $f_{VBK,0}$ . The dashed line in b) represents the experimentally obtained water solubility limit. Above the line, the copolymers were insoluble in water (regardless of the pH used) and below the line the copolymers were soluble in basic solution (pH = 9-11).

**Figure 5.** Gel permeation chromatograms of experiment a) MAA/VBK-VBK where MAA/VBK-03 is the macroinitiator (dashed black line,  $\overline{M_n} = 12.5 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.35$ ,  $F_{VBK} = 0.13$ ), MAA/VBK-VBK is the final block copolymer (solid black line,  $\overline{M_n} = 22.2$ kg·mol<sup>-1</sup>,  $\overline{M_w}/\overline{M_n} = 1.57$ ,  $F_{VBK} = 0.28$ ) and b) MAA/VBK-MMA/S-1 where MAA/VBK-B is the macroinitiator (dashed black line,  $\overline{M_n} = 3.3 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.28$ ,  $F_{VBK} = 0.16$ ), MAA/VBK-MMA/S-1 is the final block copolymer synthesized in organic solvent (solid black line,  $\overline{M_n} = 46.2 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.26$ ,  $F_{VBK} < 0.01$  and  $F_{\text{styrene}} = 0.20$ ). The experimental conditions can be found in **Table 1**.

**Figure 6.** Gel permeation chromatograms of experiment MAA/VBK-MMA/S-2 where MAA/VBK-B is the macroinitiator (dashed black line,  $\overline{M_n} = 3.3 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.28$ ,  $F_{VBK} = 0.16$ ) and MAA/VBK-MMA/S-2 is the final block copolymer synthesized by *ab initio* emulsion polymerization (solid black line,  $\overline{M_n} = 43.7 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\overline{M_w}/\overline{M_n} = 1.24$ ,  $F_{VBK} < 0.01$  and  $F_{\text{styrene}} = 0.20$ ). The experimental conditions can be found in **Table 1**.

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