Fluorescent, Thermoresponsive Oligo(ethylene glycol) Methacrylate/9-(4-vinylbenzyl)-9H-carbazole Copolymers Designed with Multiple LCSTs via Nitroxide Mediated Controlled Radical Polymerization

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Abstract

9-(4-vinylbenzyl)-9H-carbazole (VBK) was used as the "controlling" comonomer for nitroxide mediated polymerization with 10 mol% SG1 free nitroxide relative to BlocBuilder initiator at 80 ^{o}C of oligo(ethylene glycol) methyl ether methacrylate (8-9 ethylene glycol (EG) units) (OEGMA$_{8-9}$), 2-(2-methoxyethoxy)ethyl methacrylate (MEO$_2$MA) and for an OEGMA$_{8-9}$/MEO$_2$MA-mixed feed. The synthesis of MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK copolymers and MEO$_2$MA/OEGMA$_{8-9}$/VBK terpolymers exhibited linear increases in number average molecular weight ($\overline{M_n}$) versus conversion X, up until $X = 0.6$, with final copolymers characterized by relatively narrow, monomodal molecular weight distributions ($\overline{M_w}/\overline{M_n} < 1.4$, in most cases). A series of MEO$_2$MA/OEGMA$_{8-9}$/VBK terpolymers were synthesized and by varying the OEGMA$_{8-9}$:MEO$_2$MA feed ratios, the terpolymers exhibited tunable lower critical solution temperatures in water (28 °C < LCSTs < 81 °C). MEO$_2$MA/OEGMA$_{8-9}$/VBK terpolymers were deemed sufficiently pseudo-"living" to reinitiate a second batch of MEO$_2$MA/OEGMA$_{8-9}$/VBK, with few apparent dead chains, as indicated by the monomodal shift in the GPC chromatograms. The resulting MEO$_2$MA/OEGMA$_{8-9}$/VBK block copolymers were designed so that each block exhibited a distinct LCST, which was confirmed by UV-Vis and dynamic light scattering. In addition to controlling the terpolymerization, the VBK units imparted thermo-responsive fluorescence into the final copolymers.

Keywords

oligo(ethylene glycol) methyl ether methacrylates (OEGMA$_{8-9}$), 2-(2-methoxyethoxy)ethyl methacrylate (MEO$_2$MA), 9-(4-vinylbenzyl)-9H-carbazole (VBK), nitroxide mediated polymerization, block copolymer, thermoresponsive and water-soluble polymers.

Introduction

Thermo-responsive polymers undergo a sharp physical change as a response to a small change in temperature. Thermo-responsive polymers have found application in polymer drug delivery vehicles,[1,2] biochemical sensors,[3-7] environmentally-friendly photoresists,[8] intra-cellular uptake micelles,[9] and controlled-bacterial aggregation materials[10]. Thermo-responsive polymers can exhibit a lower critical solution temperature (LCST) in aqueous solution, meaning they are free flowing water-soluble chains at lower temperatures but agglomerate or precipitate out of solution above a certain temperature (i.e. the LCST). For example, poly(N-isopropyl acrylamide) (poly(NIPAAm))[11-14] and poly(2-(dimethylamino)ethyl methacrylate) (poly(DMAEMA))[15-17] exhibit LCSTs of 32 °C and 46 °C, respectively. The tuning of the polymer's LCST is highly attractive to impart more versatility and functionality into the polymer. For example, hydrophobic[18] or hydrophilic[15,19] comonomers are often incorporated into the final copolymer by statistical copolymerization to modify the LCST. Other methods of modifying LCST behaviour involve using more complex microstructures such as block copolymers or star polymers. For example, Li et al. synthesized a poly(styrene)-poly(DMAEMA)-poly(NIPAAm) star block copolymer which micellized in water and exhibited two discernable thermo-induced micellar collapses.[20] Kotsuchibashi et al. synthesized poly(NIPAAm)-*block*-poly(NIPAAm-*co*-N-(isobutoxymethyl)acrylamide) block copolymers, which underwent an initial transition from water-soluble polymers to micelles and a second transition from micelles to large aggregates when heated in an aqueous solution.[21] In these cases, the materials exhibited multiple, distinct LCSTs corresponding to the respective segments.[20,21] Several other examples of thermo-responsive block copolymers with two distinct phase transitions have been reported in the literature.[22-28]

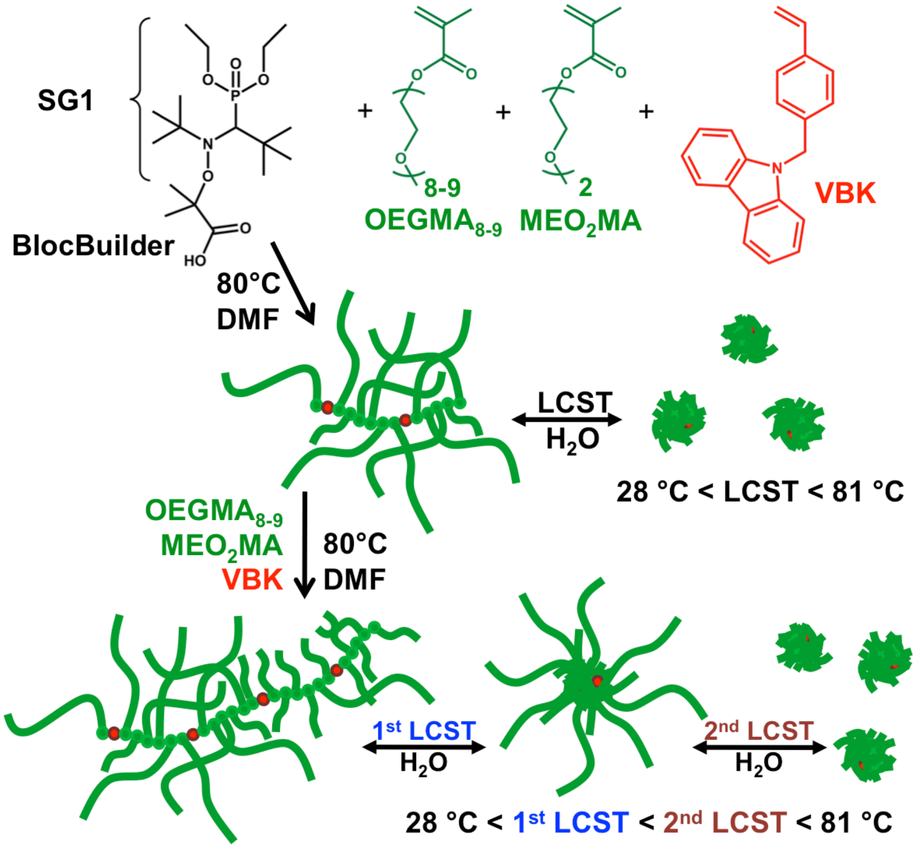
Recently, Lutz and coworkers synthesized a series of thermo-responsive copolymers based on oligo(ethylene glycol) methyl ether methacrylates with 8-9 ethylene glycol (EG) units ($\text{OEGMA}_{8\text{-}9}$) and 2-(2-methoxyethoxy)ethyl methacrylate with 2 EG units (MEO_2MA, Scheme 1).[29,30] The authors showed that by changing the ratio of $\text{OEGMA}_{8\text{-}9}$:$\text{MEO}_2\text{MA}$, a sharp and tunable LCST in water between 26 °C and 90 °C was attainable.[29,31,32] However, to obtain such well-defined LCSTs, the control of the molecular weight and copolymer composition was imperative. Lutz and coworkers used atom transfer radical polymerization (ATRP), a controlled radical polymerization (CRP) method, to synthesize $\text{OEGMA}_{8\text{-}9}$/$\text{MEO}_2\text{MA}$ copolymers to impart this composition control.[29,30] Other CRP techniques, such as reversible addition-fragmentation chain transfer (RAFT) polymerization, have also effectively controlled the molecular weight distribution and the composition of OEGMA-based copolymers.[33-36] However, the use of ATRP and RAFT can be problematic in some cases due to the presence of metallic species or thiol groups in the product, which could be detrimental in the desired application. An alternative CRP method termed nitroxide mediated controlled radical polymerization (NMP)[37,38] is a robust controlled polymerization technique that often only requires a single initiating species. Like ATRP, NMP features a reversible termination between dormant and active chains to control the radical species concentration, which in turn permits control of the molecular weight distribution and microstructure. In contrast to ATRP or RAFT, no additional purification of the final polymer is necessary prior to being used for sensitive electronic or biological applications.[37-39]

Traditionally, the major drawback of NMP was that it could only polymerize styrenics in a controlled manner. However, the development of second-generation initiating systems based on 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)[40] and [*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxidanyl (SG1, Scheme 1)[41] have permitted the homopolymerization of various monomers such as acrylates[42-45] and acrylamides[18,37] which were previously unattainable by first-generation initiating systems such as 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO). However, the homopolymerization of methacrylates by NMP was still elusive. Methacrylates have a high equilibrium constant between dormant and active chains, which result in the generation of a large number of free radicals in the initial stages of the polymerization. These radicals undergo irreversible termination characterized by a plateau of the number average molecular weight ($\bar{M}_n$) versus conversion (X).[46] The use of additional nitroxide, to quench the excess of free radicals, results in a significant increase in β–hydrogen transfer from the propagating poly(methacrylate) chain to the SG1 nitroxide, also resulting in irreversible termination.[47] However, Charleux and coworkers discovered that the use of a small amount of a "controlling" comonomer, characterized by a lower K, can be used to decrease the average equilibrium constant ($<K>$) and control the copolymerization of the methacrylate.[46,48,49] Originally the comonomer of choice was styrene, requiring 4.4-8.8 mol% relative to methyl methacrylate (MMA) to control the copolymerization.[46] The use of styrene has been successfully used to control many methacrylates such as ethyl methacrylate,[50] glycidyl methacrylate,[51] tert-butyl methacrylate,[52] benzyl methacrylate[53], methacrylic acid[54] and oligo(ethylene glycol) methyl ether methacrylates (4-5 EG units)[55,56]. While the low incorporation of styrene into the copolymer may not significantly affect the mechanical properties of the methacrylate-rich copolymer,[50] its incorporation can hinder other properties such as cell cytotoxicity[39] or water-solubility[57]. Therefore, the use of other "controlling" comonomers such as acrylonitrile (AN)[39,58,59] and 4-styrene sulfonate[57] have been introduced to eliminate such problems that arise with the use of styrene and broaden the scope of comonomer applicability. Recently, our group has introduced the use of 9-(4-vinylbenzyl)-9H-carbazole (VBK) as a "controlling" comonomer for MMA.[60] Not only did the copolymerization require as little as 1 mol% of VBK to control the copolymerization effectively, the pendant carbazole group on the VBK introduced hole-transport properties into the final copolymer.[60] VBK has also been used to control the copolymerization of DMAEMA resulting in a thermo/pH responsive, fluorescent copolymer.[18]

Nicolas and coworkers have recently shown that the controlled copolymerization of oligo(ethylene glycol) methyl ether methacrylates (4-5 EG units) and acrylonitrile is possible by using an SG1-based alkoxyamine, 2-([tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxy)-2-methylpropionic acid unimolecular initiator (BlocBuilder) in an ethanol/water solution at 71-85 °C, resulting in polymers with low polydispersity that were water-soluble and biocompatible.[39] Schubert and coworkers synthesized OEGMA$_{8-9}$-based copolymers using pentafluorostyrene (PFS) as a "controlling" comonomer, resulting in final statistical copolymers with various PFS:OEGMA$_{8-9}$ ratios and relatively narrow molecular weight distributions ($\overline{M_w}/\overline{M_n}$ =1.22-1.73).[61] While considerable research in the field of thermo-responsive pendent-EG based acrylates has been accomplished using NMP,[28,62] very little literature can be found concerning the polymerization of MEO$_2$MA, OEGMA$_{8-9}$ or a mixture of MEO$_2$MA with OEGMA$_{8-9}$ by NMP.[61]

In this study, VBK was used to copolymerize OEGMA$_{8-9}$ and MEO$_2$MA with varying amounts of VBK in the feed ($f_{VBK,0}$ = 0.01-0.20). The effect of feed composition on kinetics, polymerization control and final composition will be discussed. Secondly, a series of MEO$_2$MA/OEGMA$_{8-9}$/VBK terpolymers, with various MEO$_2$MA/OEGMA$_{8-9}$ ratios (while keeping the VBK content constant) were synthesized and their LCSTs in water were determined (Scheme 1). The effect of temperature on the terpolymer fluorescence was also investigated. Finally, characteristic terpolymers were used as macroinitiators to re-initiate a fresh batch of

$MEO_2MA/OEGMA_{8-9}/VBK$ ternary mixtures, resulting in a double thermo-responsive block copolymer (Scheme 1). These findings illustrate the versatility of NMP and its ability to synthesize potentially biocompatible, fluorescent block copolymers with tunable multi-LCSTs, which could find application in next-generation sensors or drug delivery vehicles.



Scheme 1. Terpolymerization of 2-(2-methoxyethoxy)ethyl methacrylate (MEO_2MA), oligo(ethylene glycol) methyl ether methacrylate ($OEGMA_{8-9}$) and 9-(4-vinylbenzyl)-9H-carbazole (VBK) by nitroxide mediated polymerization using BlocBuilder, followed by a subsequent chain extension of the final thermo-responsive terpolymer with a fresh batch of VBK, MEO_2MA and $OEGMA_{8-9}$ (with a different $MEO_2MA:OEGMA_{8-9}$ compared to the first block) resulting in a block copolymer that exhibits dual lower critical solution temperatures (LCST) in water.

EXPERIMENTAL

Materials

N,N-Dimethylformamide (DMF, >95%, certified ACS), ethyl ether (anhydrous, >95%, BHT stabilized/certified ACS) and tetrahydrofuran (THF, >99.5%, HPLC grade) were obtained from Fisher Scientific and used as received. Deuterated chloroform ($CDCl_3$, >99%), used for ^1H NMR spectroscopy, was obtained from Cambridge Isotopes Laboratory and also used as received. 2-(2-Methoxyethoxy)ethyl methacrylate, also known as di(ethylene glycol) methyl ether methacrylate (MEO_2MA, 188 $g \cdot mol^{-1}$, 95%, 100 ppm hydroquinone monomethyl ether as inhibitor) and oligo(ethylene glycol) methyl ether methacrylate ($OEGMA_{8-9}$, average molecular weight $\overline{M_n}$ = 475 $g \cdot mol^{-1}$, contained 100 ppm MEHQ as inhibitor and 300 ppm BHT as inhibitor) were obtained from Sigma-Aldrich and used as received. 9-(4-Vinylbenzyl)-9H-carbazole (VBK, >95%) was synthesized according to the literature.[63] 2-([*tert*-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxy)-2-methylpropanoic acid (BlocBuilder-MA^{TM}, 99%) and [*tert*-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxidanyl (SG1, >85%) were obtained from Arkema and used without further purification.

Random Copolymerization of 2-(2-Methoxyethoxy)Ethyl Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole (MEO_2MA/VBK) and Oligo(Ethylene Glycol) Methyl Ether Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole ($OEGMA_{8-9}$/VBK).

All MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymerizations were performed in a 50 mL three-neck round bottom glass reactor equipped with a condenser (cooled with a 50 vol % ethylene glycol to water mixture being circulated using a Neslab 740 chiller). The reactor temperature was modulated using a heating mantle connected to a temperature controller, which measured the temperature inside the reactor with a thermocouple located in the thermal well, also connected to the reactor. Once assembled, the reactor was filled with the reagents and a stir bar, prior to being placed on a magnetic stir plate. All copolymerizations were done in 50 wt % DMF solution with target number average molecular weight of 25 kg·mol^{-1} at complete conversion and with varying amounts of VBK relative to MEO$_2$MA or OEGMA$_{8-9}$ (initial molar feed composition of VBK of $f_{VBK,0}$ = 0.01-0.20). All experimental formulations can be found in Table 1. As an example, the synthesis of MEO$_2$MA/VBK-5 is shown as an example. To the reactor was added VBK (0.46 g, 1.7 mmol), MEO$_2$MA (6.10 g, 32.4 mmol), BlocBuilder (0.10 g, 0.26 mmol), SG1 (0.008 g, 0.03 mmol) and DMF (15.5 g). The condenser and the third opening of the reactor were sealed using a rubber septum prior to inserting a needle and bubbling the mixture for 30 minutes with ultra pure nitrogen. The reactor was then heated with a heating rate of 10 °C·min^{-1}, while maintaining a light nitrogen purge, until the temperature reached 80 °C. The "start" of the copolymerization, t = 0 min, was arbitrarily assigned as the time when the reactor temperature reached 80 °C. Samples were periodically drawn from the reactor by syringe and characterized by GPC and ^{1}H NMR spectroscopy without further purification. After cooling, the crude product was separated from the monomer by dialysis (membrane MWCO = 3500 g·mol^{-1}, Spectrum Laboratories) against water for a week. The recovered polymer was then dried in a vacuum oven at 60 °C to remove the residual solvent. For the specific example cited, the final copolymer was characterized by a yield of 2.49 g (conversion X = 0.49, determined by ^{1}H NMR spectroscopy) with number average molecular weight, $\bar{M}_n$ = 12.1 kg·mol^{-1}, a polydispersity index of $\overline{M_w}/\overline{M_n}$= 1.34 (determined by gel permeation chromatography (GPC) using THF as an eluent at 40 °C and poly(styrene) standards) and a final molar VBK copolymer composition of F_{VBK} = 0.08 (determined by ^{1}H NMR spectroscopy).

Terpolymerization of 2-(2-Methoxyethoxy)Ethyl Methacrylate (MEO_2MA), Oligo(Ethylene Glycol) Methyl Ether Methacrylate ($OEGMA_{8-9}$) and 9-(4-Vinylbenzyl)-9H-Carbazole (VBK).

All $MEO_2MA/OEGMA_{8-9}$/VBK terpolymerizations were performed in an identical setup as the MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymerizations and by following the identical procedure as the copolymerizations. The terpolymerizations were done in 50 wt % DMF solution with target number average molecular weights of 25 - 425 kg·mol $^{-1}$ and all the corresponding formulations can be found in Table 2. For the terpolymerizations, the amount of VBK was kept constant ($f_{VBK,0}$ = 0.02), while the amounts of MEO_2MA relative to $OEGMA_{8-9}$ were varied for all terpolymerizations. As an example, the synthesis of OM40/60 was performed by adding VBK (0.10 g, 0.37 mmol), MEO_2MA (2.07 g, 11.0 mmol), $OEGMA_{8-9}$ (3.27 g, 7.27 mmol), BlocBuilder (0.034 g, 0.89 mmol), SG1 (0.003 g, 0.01 mmol) and DMF (8.50 g) to the reactor followed by nitrogen bubbling of 30 minutes. The mixture was then heated to 80 °C and samples were drawn periodically by syringe. The final product was separated from the unreacted monomer by osmosis (membrane MWCO = 3500 g·mol^{-1}, Spectrum Laboratories) against water for a week and dried in the vacuum oven at 60 °C to remove the residual solvent. For the specific example cited, the final copolymer was characterized by a yield, after transfer losses from the dialysis and recovery, of 1.48 g (X = 0.49) with $\overline{M_n}$ = 28.7 kg·mol^{-1}, $\overline{M_w}/\overline{M_n}$ = 1.34 (determined by GPC using THF as an eluent and poly(styrene) standards), $F_{VBK} < 0.01$ and $F_{MEO2MA} = 0.68$ (final composition determined by ^{1}H NMR spectroscopy).

Chain Extension of 2-(2-Methoxyethoxy)Ethyl Methacrylate, Oligo(Ethylene Glycol) Methyl Ether Methacrylate and 9-(4-Vinylbenzyl)-9H-Carbazole (MEO$_2$MA/OEGMA$_{8-9}$/VBK) Terpolymers with a fresh batch of MEO$_2$MA/OEGMA$_{8-9}$/VBK

All MEO$_2$MA/OEGMA$_{8-9}$/VBK chain extensions were performed in an identical setup and by following the identical procedure to the copolymerizations and terpolymerizations. Similar to the terpolymerizations, the amounts of MEO$_2$MA relative to OEGMA$_{8-9}$ were varied all while keeping the amount of VBK constant ($f_{VBK,0} = 0.02$) for all chain extension polymers. However, the ratios of MEO$_2$MA:OEGMA$_{8-9}$ for each block were manipulated so as to attain a different LCST for each block. All the corresponding formulations can be found in Table 2. As an example, the synthesis of OM10/90-OM50/50 was performed by adding VBK (0.05 g, 0.16 mmol), MEO$_2$MA (0.85 g, 4.52 mmol), OEGMA$_{8-9}$ (2.05 g, 7.27 mmol), DMF (4.3 g) and the macroinitiator (OM10/90, 0.11 g, 0.006 mmol, $\overline{M_n} = 18.5$ kg·mol^{-1} and $\overline{M_w}/\overline{M_n} = 1.55$, see Table 2 and Table 4 for full characterization data of the macroinitator) to the reactor. The mixture was bubbled with nitrogen for 30 minutes prior to being heated to 80 °C. Thereafter, samples were drawn periodically by syringe and used for monitoring the chain growth. After cooling, the final samples were separated from the MEO$_2$MA/OEGMA$_{8-9}$ monomers by osmosis (membrane MWCO = 3500 g·mol^{-1}, Spectrum Laboratories) against water for 4 days followed by vacuum filtration to remove the unreacted VBK. OM10/90-OM50/50: yield of 0.1 g with $\overline{M_n} = 35.2$ kg·mol^{-1}, $\overline{M_w}/\overline{M_n} = 1.69$ (determined by GPC using THF as an eluent and poly(styrene) standards), $F_{VBK} = 0.04$, $F_{MEO2MA} =$

0.91 and $F_{OEGMA8\text{-}9}$ = 0.05 (final composition determined by ^{1}H NMR spectroscopy). The low yield is a result of the transfer losses from the reactor to dialysis membrane and from the dialysis membrane to the final storage vial.

Characterization

The molecular weight distribution was measured using gel permeation chromatography (GPC, Water Breeze) with THF as the mobile phase, which was run at a flow rate of 0.3 mL min^{-1}. The GPC was equipped with a guard column and with 3 Waters Styragel® HR columns (HR1 with molecular weight measurement range of 0.1 to 5 kg·mol^{-1}, HR2 with molecular weight measurement range of 0.5 to 20 kg·mol^{-1} and HR4 with molecular weight measurement range 5 to 600 kg·mol^{-1}), which were heated to 40 ºC during the analysis. The GPC was equipped with both ultra-violet (UV 2487) and differential refractive index (RI 2410) detectors. The molecular weights were determined by calibration against linear, nearly monodisperse poly(styrene) standards. Final copolymer composition was estimated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were obtained using a 200 MHz Varian Gemini 2000 spectrometer using $CDCl_3$ solvent in 5 mm Up NMR tubes and by performing a minimum of 32 scans per sample. The copolymer composition was determined by the ratio of the methylene protons corresponding to VBK units (δ = 5.2–5.4 ppm, Ar-CH_2-N-) and the resonances corresponding to the proton adjacent to the ester next to the backbone of the methacrylate (δ = 4.0–4.1 ppm, O-CH_2-CH_2) for MEO_2MA and for $OEGMA_{8\text{-}9}$). For the terpolymers, the composition of MEO_2MA, $OEGMA_{8\text{-}9}$ and VBK was determined by comparing the signal due to protons adjacent to the ester next to the backbone of the methacrylate (δ = 4.0–4.1 ppm, O-CH_2-CH_2, 2H for MEO_2MA and 2H for $OEGMA_{8\text{-}9}$), the protons adjacent to the ester within the repeat unit of EG of the methacrylate (δ = 3.5-3.75 ppm, -CH_2-O-[-CH_2-CH_2-

0-]$_n$-, 6H for MEO$_2$MA and 34H for OEGMA$_{8\text{-}9}$) and the methylene protons corresponding to the VBK units (δ = 5.2–5.4 ppm, Ar-CH_2-N-). The individual monomer conversion was determined by comparing the vinyl peaks (δ = 6.6, 5.6 and 5.1 ppm for VBK and δ = 5.45 and 6.05 ppm for OEGMA$_{8\text{-}9}$ and MEO$_2$MA) of the respective monomers, to the methoxy group (δ = 4.0 and 4.1 ppm, for OEGMA$_{8\text{-}9}$ and MEO$_2$MA) and the methylene group (δ = 5.2–5.4 ppm, corresponding to the VBK) corresponding to the respective monomers and copolymers. The overall monomer conversion (X) for the MEO$_2$MA/VBK and OEGMA$_{8\text{-}9}$/VBK copolymerizations was then determined by Equation 1:

$$X = f_{VBK,0}X_{VBK} + f_{OEGMA8\text{-}9,0}X_{OEGMA8\text{-}9} \text{ and } X = f_{VBK,0}X_{VBK} + f_{MEO2MA,0}X_{MEO2MA} \qquad \text{Equation 1}$$

where X_{VBK}, $X_{OEGMA8\text{-}9}$, X_{MEO2MA} are the individual monomer conversions for VBK, OEGMA$_{8\text{-}9}$ and MEO$_2$MA, respectively and $f_{VBK,0}$, $f_{MEO2MA,0}$ and $f_{OEGMA8\text{-}9,0}$ are initial mol fractions in the feed for VBK, OEGMA$_{8\text{-}9}$ and MEO$_2$MA, respectively. Cloud point temperatures (CPTs) were determined by dynamic light scattering (DLS) and UV-Vis spectroscopy from 3 g·L^{-1} solutions of terpolymer in neutral water (purified by reverse osmosis). DLS measurements were performed with a Malvern Zetasizer Nano equipped with a 532 nm 50 mW green laser. For the terpolymers, the samples were heated in 1 °C increments, allowed to equilibrate for 1 minute followed by 12 measurements, which were then averaged together to give one value at the temperature of interest (average heat cycle ≈ 6-8 hours). For the poly(MEO$_2$MA-*ran*-OEGMA$_{8\text{-}9}$-*ran*-VBK)-*block*-poly(MEO$_2$MA-*ran*-OEGMA$_{8\text{-}9}$-*ran*-VBK) block copolymers, the samples were heated in increments of 0.2 °C, allowed to equilibrate for 1 minute followed by 10 measurements, which were averaged together to give one value at the corresponding temperature (average heat cycle ≈ 14-16 hours). The CPTs for the terpolymers were taken once the scaled Z-average diameter reached 0.5 and was reported as the average of three experiments. The dual CPTs for the poly(MEO_2MA-*ran*-$OEGMA_{8-9}$-*ran*-VBK)-*block*-poly(MEO_2MA-*ran*-$OEGMA_{8-9}$-*ran*-VBK) block copolymers were estimated as the temperature of the midpoint between the measurement plateau. UV–Vis measurements were performed with a Cary 5000 UV–Vis-NIR spectrometer (Agilent Technologies) equipped with a Peltier thermostatted (6 × 6) multi-cell holder equipped with temperature controller and magnetic stirring. Using a heating rate of 0.5 °C min^{-1}, the CPT was taken once the scaled absorbance, at 500 nm, reached 0.5. Fluorescence measurements were performed with a Cary Eclipse Fluorescence Spectrophotometer equipped with a xenon flash lamp and Peltier thermostatted (4) multicell holder with temperature controller. Quartz cuvettes filled with 3 mg L^{-1} solutions were excited at a wavelength of 330 nm at various temperatures.

RESULTS AND DISCUSSION

Prior to synthesizing a $MEO_2MA/OEGMA_{8-9}$/VBK terpolymer, a better understanding of the effect of VBK on its respective copolymerization with MEO_2MA and of $OEGMA_{8-9}$ by NMP was required. Therefore, a series of MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymers with various $f_{VBK,0}$ were synthesized at 80 °C (Table 1). The molecular weight characteristics, the final copolymer composition and the water-solubility of the poly(VBK-*ran*-MEO_2MA) and poly(VBK-*ran*-$OEGMA_{8-9}$) copolymers are summarized in Table 3.

Kinetics of the Random Copolymerizations of 2-(2-Methoxyethoxy)Ethyl Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole (MEO_2MA/VBK) and Oligo(Ethylene Glycol) Methyl Ether Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole ($OEGMA_{8-9}$/VBK)

The average equilibrium constant, <K>, is defined in terms of the concentration of propagating macroradicals [P•], free nitroxide [N•] and the dormant alkoxyamine terminated species [P-N] (Equation 2).

$$\langle K \rangle = \frac{[P\bullet][N\bullet]}{[P-N]} \qquad \text{Equation 2}$$

An average equilibrium constant is used since the polymerization is a statistical copolymerization consisting of two monomers, which may have very different individual equilibrium constants. The semi-logarithmic kinetic plots of $\ln[(1-X)^{-1}]$ versus time for MEO_2MA/VBK and $OEGMA_{8-9}$/VBK are illustrated in Figure 1a and Figure 1b, respectively. The apparent rate constant, <k_P>[P•], which is the product of <k_P>, the average propagation rate constant, and [P•], the concentration of propagating macro-radicals, was determined from the slopes found in Figure 1, calculated typically from about 4-5 sample points taken in the linear region of the $\ln[(1-X)^{-1}]$ versus time plots. Generally, in the early stages of the polymerization, it can be assumed that the initial concentration of nitroxide $[N\bullet]_0$ is sufficiently high so that $[N\bullet] = [N\bullet]_0$ and that [P-N] is approximately equal to the initial concentration of initiator ($[P\text{-}N] = [\text{BlocBuilder}]_0$). By taking these assumptions into account, the apparent rate constant can be related to the <K> as the product <k_P><K>. Equation 2 thus is converted to the following form where r is the initial molar ratio of free nitroxide relative to BlocBuilder initiator ($r = [\text{SG1}]_0/[\text{BlocBuilder}]_0$) after multiplying Equation 2 by <k_P>.

$$\langle k_P \rangle \langle K \rangle \cong \langle k_P \rangle \frac{[P\bullet][SG1]_0}{[BlocBuilder]_0} = \langle k_P \rangle [P\bullet] r \qquad [3]$$

For the systems studied here, the $<k_P>$[P•] reported were taken during the early stages of polymerization where linear growth of $\overline{M}_n$ versus conversion was observed (typically during the first 60 minutes of the polymerization where the previously mentioned assumptions held reasonably well). The experimental $<k_P><K>$ values obtained for the MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK copolymerizations were compared and are summarized in Table 4. The experimental $<k_P><K>$ tended to decrease slightly with increasing initial feed composition of VBK. For example, with $f_{VBK,0}$ = 0.01, $<k_P><K>_{\mathrm{MEO2MA/VBK}}$ = $(2.2 \pm 0.2) \times 10^{-6}$ s^{-1} and $<k_P><K>_{\mathrm{OEGMA8\text{-}9/VBK}}$ = $(3.0 \pm 0.4) \times 10^{-6}$ s^{-1}. At a higher $f_{VBK,0}$ = 0.10, $<k_P><K>_{\mathrm{MEO2MA/VBK}}$ = $(1.6 \pm 0.2) \times 10^{-6}$ s^{-1} and $<k_P><K>_{\mathrm{OEGMA8\text{-}9/VBK}}$ = $(9.6 \pm 0.9) \times 10^{-7}$ s^{-1} (see Table 4 for all $<k_P><K>$). This observation was previously reported for MMA/VBK copolymerizations and is due to the low k_PK associated with VBK homopolymerizations at 80 °C.[60] The general increase in $<k_P><K>$ as a function of decreasing VBK content suggested the polymerizations were becoming less controlled and this was reflected in higher polymerization rates (Table 4) and generally broader molecular weight distributions (Table 3). It appears that regardless of the VBK content in the feed, there is no significant difference between $<k_P><K>_{\mathrm{OEGMA8\text{-}9/VBK}}$ and $<k_P><K>_{\mathrm{MEO2MA/VBK}}$. As a comparison, MMA/VBK copolymerization done in a dilute DMF solution at 80 °C with $f_{VBK,0}$ = 0.05 resulted in $<k_P><K>_{\mathrm{MMA/VBK}}$ = $(5.4 \pm 0.1) \times 10^{-6}$ s^{-1}.[60] Similarly, DMAEMA/VBK copolymerization in DMF at 80 °C with $f_{VBK,0}$ = 0.05 also resulted in $<k_P><K>_{\mathrm{DMAEMA/VBK}}$ = $(5.4 \pm 0.3) \times 10^{-6}$ s^{-1}.[18] Therefore, the $<k_P><K>$ of MMA/VBK and DMAEMA/VBK is roughly 2 times greater than $<k_P><K>_{\mathrm{MEO2MA/VBK}}$ and $<k_P><K>_{\mathrm{OEGMA8\text{-}9/VBK}}$, when the copolymerization is performed in DMF at 80 °C with $f_{VBK,0}$ = 0.05. As mentioned earlier, $<k_P>$ is an average of k_Ps corresponding to the respective monomers being copolymerized. Literature values for k_P of some oligo(ethylene glycol) methacrylates have been previously determined using pulsed laser polymerization (PLP) and can be used to make comparisons with respect to $<k_P><K>$. The k_P corresponding to MEO$_2$MA done in bulk at 80 °C is $k_{P,\ \mathrm{MEO2MA,80°C}}$ = 1460 L·mol^{-1}·s^{-1},[64] and is very similar to that of MMA done in bulk at 80 °C, $k_{P,\ \mathrm{MMA,80°C}}$ = 1297 L·mol^{-1}·s^{-1}.[65] These values suggest that K_{MEO2MA} must therefore be not very different compared to K_{MMA}, when polymerized in DMF at 80 °C. It has been reported that as the size of the EG chain increases, the corresponding k_P's also increase.[64] For example, the k_P corresponding to OEGMA$_3$ (oligo(ethylene glycol) methyl ether methacrylate with 3 EG units) done in bulk at 80 °C has $k_{P,\mathrm{OEGMA3,80°C}}$ = 2270 L·mol^{-1}·s^{-1}.[64] However, no k_P for OEGMA$_{8\text{-}9}$ has been reported and therefore any comparison drawn between K_{MEO2MA} and $K_{\mathrm{OEGMA8\text{-}9}}$ would be speculative.

The use of VBK as a "controlling" comonomer for MEO$_2$MA and OEGMA$_{8\text{-}9}$ resulted in a linear increase in $\overline{M_n}$ versus X up until $X = 0.6$, regardless of the $f_{VBK,0}$ used (Figure 1b and d). The growth in chains can be easily monitored by the shift in GPC chromatograms (see supporting information, Figure S1). The decrease in OEGMA$_{8\text{-}9}$ monomer concentration also appears in the GPC chromatograms due to its relatively high molecular weight (Figure S1, observe the peaks at an elution time of ≈ 32 min). In the case of MEO$_2$MA/VBK using $f_{VBK,0} = 0.01$, the experimentally obtained $\overline{M_n}$ was slightly higher than the theoretical $\overline{M_n}$ and the copolymerizations experienced a slight broadening of the molecular weight distribution ($\overline{M_w}/\overline{M_n} \approx 1.6$), indicating a decrease in apparent initiator efficiency. Also, there is an offset at early polymerization time, suggesting chains were rapidly being formed, and there was not enough comonomer to provide sufficient control. Similar decreases in initiator efficiencies have been previously reported for the copolymerization of MMA/S[46] and MMA/VBK[60], as the concentration of "controlling" comonomer was decreased. In the case of OEGMA$_{8\text{-}9}$/VBK using $f_{VBK,0} = 0.01$, the experimentally obtained $\overline{M_n}$ does not appear to follow the theoretical $\overline{M_n}$. However, the molecular weight distribution remained relatively narrow ($\overline{M_w}/\overline{M_n} \leq 1.3$). For MMA/VBK copolymerizations, the use of 1 mol% VBK relative to MMA seemed to be the lowest VBK feed concentration that could be feasibly used to obtain a controlled polymerization.[60] For the copolymerizations of MEO_2MA/VBK and $OEGMA_{8-9}$/VBK, it appears that 1 mol% VBK in the feed is not sufficient to keep the polymerization controlled completely. Both the MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymerizations were characterized by linear growth of $\overline{M_n}$ versus X and by final copolymers characterized by narrow molecular weight distributions with $\overline{M_w}/\overline{M_n} < 1.4$ as long as $f_{VBK,0} > 0.01$.

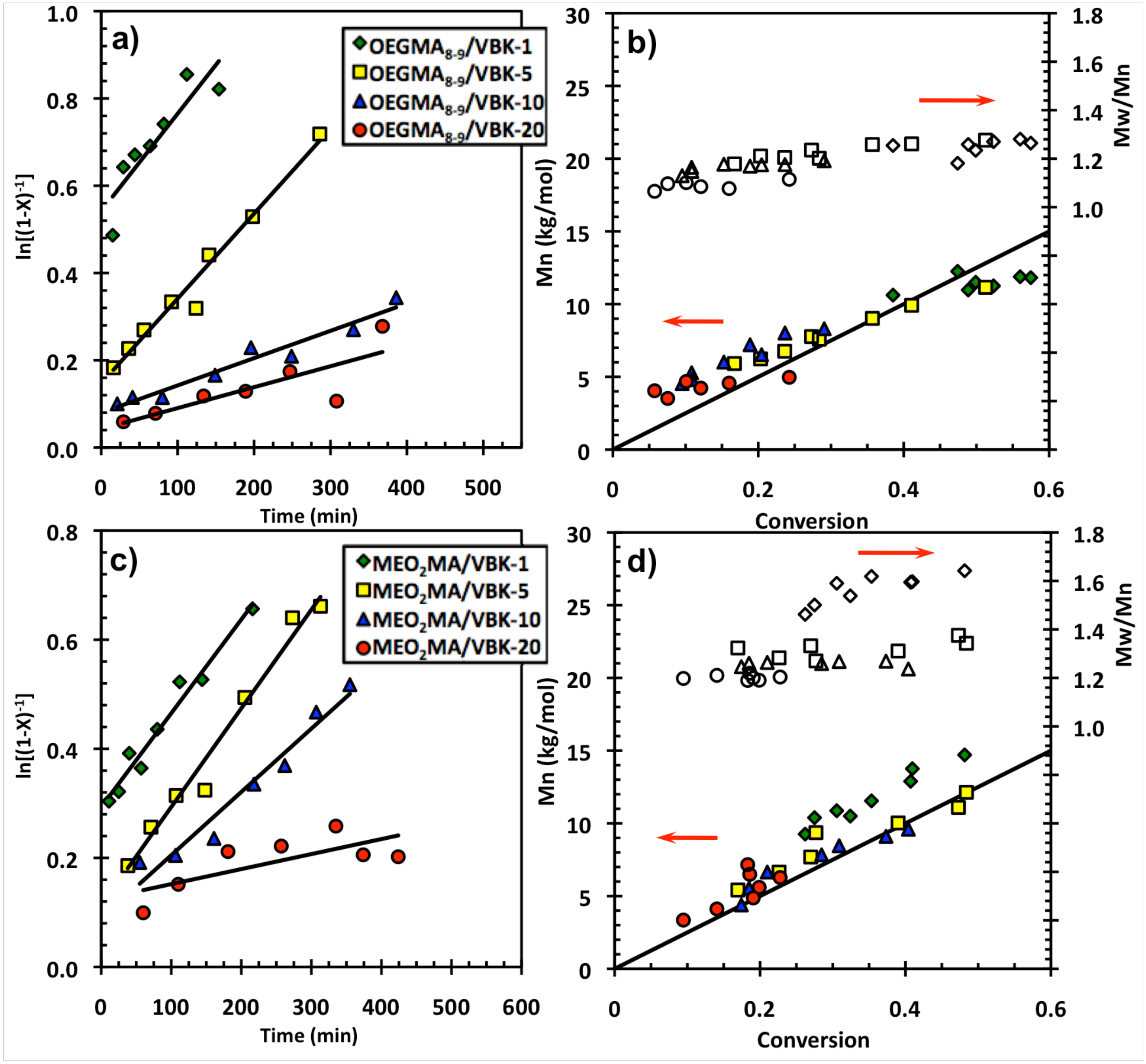


Figure 1. (a) and (c) show semi-logarithmic plot of conversion ($\ln((1 - X)^{-1})$ (X = conversion) versus time for 2-(2-methoxyethoxy)ethyl methacrylate9-(4-vinylbenzyl)-9H-carbazole (MEO$_2$MA/VBK) and oligo(ethylene glycol) methyl ether methacrylate/VBK (OEGMA$_{8-9}$/VBK) copolymerizations, respectively, as functions of different initial feed compositions. In (b) and (d), the number-average molecular weight $\overline{M_n}$ versus X for MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK copolymerizations are shown, respectively. The legend in a) corresponds to the experiments displayed in both a) and b), while, the legend in c) corresponds to the experiments in c) and d).

The empty symbols in b) and d) correspond to the $\overline{M_w}/\overline{M_n}$ versus X for the respective copolymerization corresponding to the respective filled symbol.

2-(2-Methoxyethoxy)Ethyl Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole (MEO$_2$MA/VBK) and Oligo(Ethylene Glycol) Methyl Ether Methacrylate with 9-(4-Vinylbenzyl)-9H-Carbazole (OEGMA$_{8-9}$/VBK) Statistical Copolymerizations: Copolymer Composition

Since the nitroxide-mediated copolymerization of MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK has not been studied using the BlocBuilder/SG1 initiating system, it was necessary to uncover the effect of feed composition on the copolymer composition. The results would then be useful for subsequent tailoring of copolymer composition, which is expected to have a strong effect on the water-solubility of the final copolymer. Several MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK copolymerizations were carried out while varying $f_{VBK,0}$ between 0.01 to 0.2 (Table 1). As previously mentioned, the copolymer composition was determined by ^{1}H NMR spectroscopy. Table 3 indicates the compositions of the various MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK random copolymers synthesized with various initial feed formulations. Generally, the composition of VBK is richer in the copolymer than in the initial copolymerization feed (Table 3). The preferential addition of VBK relative to MEO$_2$MA or OEGMA$_{8-9}$ is consistent with the observations for VBK/MMA[60] and VBK/DMAEMA[18] copolymerizations. The composition of copolymer samples taken early in the MEO$_2$MA/VBK and OEGMA$_{8-9}$/VBK copolymerizations ($X < 0.2$) were plotted as a function of feed composition (Figure 2). As a comparison, the copolymer composition of MMA/VBK was fit to a terminal model (e.g.: Mayo-Lewis equation[66]) using reactivity ratios, r_{MMA}

= 0.24 ± 0.14 and r_{VBK} = 2.7 ± 1.5, which were previously determined for MMA/VBK copolymers by NMP using the identifical initiator system, solvent and polymerization temperature.[60] The terminal model for MMA/VBK is represented in Figure 2 as the dashed line. It is evident that, for the composition range studied ($f_{VBK,0}$ = 0.01 - 0.20), MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymerizations were behaving in a similar fashion to the MMA/VBK copolymerization, illustrated by a preferential addition of VBK to itself, with regards to the respective methacrylate. For the purpose of this study, oligo-methacrylate-rich copolymers and terpolymers were synthesized with low $f_{VBK,0}$ to maintain water-solubility. As previously mentioned, very little VBK in the feed was necessary to be effective as a methacrylate-"controlling" comonomer and to impart fluorescence ($f_{VBK,0}$ = 0.01-0.05).[18,60] However, too much VBK in the feed resulted in a water-insoluble product ($F_{VBK,0}$ > 0.07 yielded water-insoluble copolymers)[18].

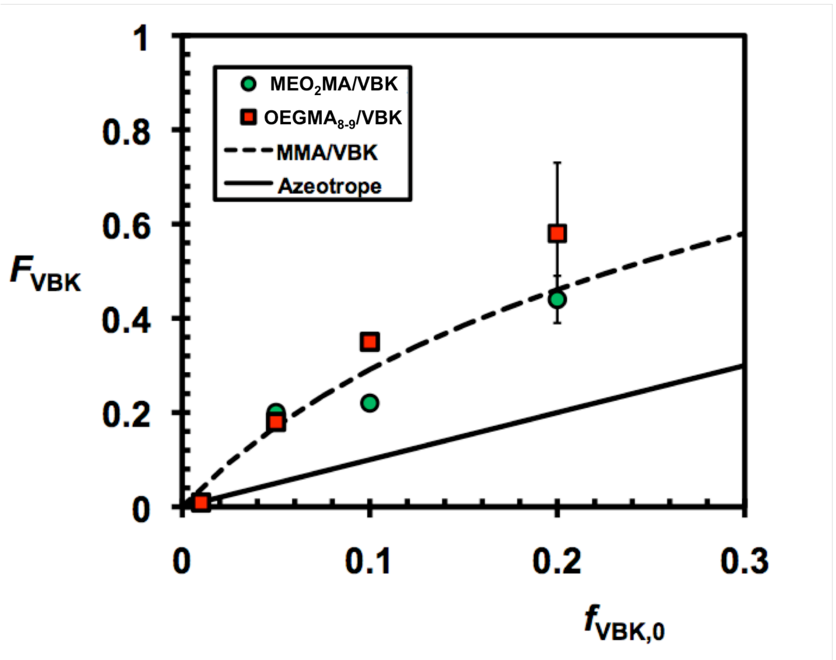


Figure 2. 9-(4-vinylbenzyl)-9H-carbazole (VBK) copolymer composition F_{VBK} with respect to initial VBK feed composition $f_{VBK,0}$ for various methacrylate/VBK copolymerizations at 80 °C in

dimethylformamide (DMF). Experimentally obtained compositions for 2-(2-methoxyethoxy)ethyl methacrylate/VBK (MEO_2MA/VBK) copolymers and oligo(ethylene glycol) methyl ether methacrylate/VBK ($OEGMA_{8-9}$/VBK) copolymers are represented by the circles and squares, respectively. The dashed line represents the theoretical fit to a terminal model (Mayo-Lewis equation) using $r_{MMA} = 0.24 \pm 0.14$ and $r_{VBK} = 2.7 \pm 1.5$, which were previously determined for methyl methacrylate/VBK copolymerizations (MMA/VBK)[60]. The solid line represents the azeotropic composition ($r_{MMA} = r_{VBK} = 1$).

Controlled Terpolymerization of 2-(2-Methoxyethoxy)Ethyl Methacrylate, Oligo(Ethylene Glycol) Methyl Ether Methacrylate and 9-(4-Vinylbenzyl)-9H-Carbazole (MEO_2MA/$OEGMA_{8-9}$/VBK)

As mentioned in the previous section, the MEO_2MA/VBK and $OEGMA_{8-9}$/VBK binary copolymerizations resulted in a controlled copolymerization as long as $f_{VBK,0} > 0.01$. Therefore, a series of MEO_2MA/$OEGMA_{8-9}$/VBK terpolymers were synthesized at 80 °C (Table 2), with variable feed ratios of MEO_2MA:$OEGMA_{8-9}$ while keeping the VBK composition constant but sufficiently high to ensure good control ($f_{VBK,0} = 0.02$). The terpolymers were targeted since varying the MEO_2MA:$OEGMA_{8-9}$ ratio permitted tuning of the LCST. The molecular weight characteristics and the final composition for the poly(VBK-*ran*-MEO_2MA-*ran*-$OEGMA_{8-9}$) random terpolymers are found in Table 5. The final terpolymers were characterized by relatively narrow molecular weight distributions with $\overline{M_w}/\overline{M_n}$= 1.20-1.58 and $\overline{M_n}$ = 12.0-47.7 kg·mol^{-1} (Table 5). A characteristic scaled conversion ($\ln(1-X)^{-1}$) versus polymerization time and $\overline{M_n}$ versus X plot for a terpolymerization (OM20/80) are depicted in Figure 3a and Figure 3b, respectively. While only three samples were taken during the course of the terpolymerization, it appears that $\bar{M}_n$ increased linearly with X (up to $X \approx 0.6$) and that the $\overline{M_w}/\overline{M_n}$ remained relatively low with $\overline{M_w}/\overline{M_n} < 1.30$. The corresponding GPC chromatograms depict the $\overline{M_n}$ growth with time (Figure 3c). It would appear that the MEO$_2$MA/OEGMA$_{8\text{-}9}$/VBK terpolymerization was behaving in a similar fashion to the MEO$_2$MA/VBK and OEGMA$_{8\text{-}9}$/VBK binary copolymerizations. The use of as little as $f_{VBK,0} = 0.02$ resulted in a controlled terpolymerization of MEO$_2$MA/OEGMA$_{8\text{-}9}$/VBK by NMP using the BlocBuilder/SG1 initiating system. Similar to the MEO$_2$MA/VBK and OEGMA$_{8\text{-}9}$/VBK copolymerizations, VBK can be used as a "controlling" comonomer for the terpolymerization of DEGM/OEGMA$_{8\text{-}9}$/VBK and was characterized by narrow molecular weight distributions for a wide range of OEGMA$_{8\text{-}9}$:MEO$_2$MA ratios (Table 5).

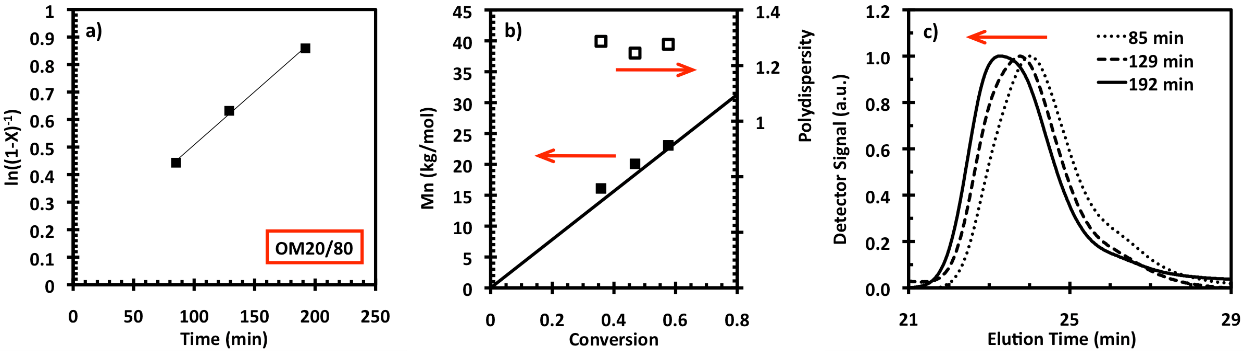


Figure 3. Characteristic (a) semi-logarithmic plot of conversion ($\ln((1 - X)^{-1})$ (X = conversion) versus time, (b) number-average molecular weight $\overline{M_n}$ versus X and (c) gel permeation chromatograms for the terpolymerization of 2-(2-methoxyethoxy)ethyl methacrylate/oligo(ethylene glycol) methyl ether methacrylate/9-(4-vinylbenzyl)-9H-carbazole (MEO$_2$MA/OEGMA$_{8\text{-}9}$/VBK). The synthesis represented here is OM20/80 and its formulation can be found in Table 2 while the terpolymer characterization is summarized in Table 5.

Chain Extension of 2-(2-Methoxyethoxy)Ethyl Methacrylate, Oligo(Ethylene Glycol) Methyl Ether Methacrylate and 9-(4-Vinylbenzyl)-9H-Carbazole ($MEO_2MA/OEGMA_{8\text{-}9}/VBK$) Terpolymers

A series of characteristic $MEO_2MA/OEGMA_{8\text{-}9}/VBK$ terpolymers were used to re-initiate a fresh batch of $MEO_2MA/OEGMA_{8\text{-}9}/VBK$ in DMF at 80 °C (see Table 2 for formulations). The molecular weight characteristics of the poly(MEO_2MA-*ran*-$OEGMA_{8\text{-}9}$-*ran*-VBK)-*block*-poly(MEO_2MA-*ran*-$OEGMA_{8\text{-}9}$-*ran*-VBK) block copolymers are found in Table 5. The terpolymer macroinitiators underwent an increase in $\overline{M}_n$ from 12.0-39.2 $kg{\cdot}mol^{-1}$ to 35.2-91.9 $kg{\cdot}mol^{-1}$ after chain extension and their molecular weight distributions broadened with from $\overline{M}_w/\overline{M}_n$= 1.20-1.69 to 1.30-1.95 (Table 5). The $\overline{M}_n$ increased linearly versus conversion while the $\overline{M}_w/\overline{M}_n$ remained relatively low ($\overline{M}_w/\overline{M}_n \approx 1.3$), illustrating the controlled behavior of the polymerization of OM5/95-OM50/50, a characteristic chain extension of $MEO_2MA/OEGMA_{8\text{-}9}/VBK$ terpolymer (Figure 4). The GPC chromatograms exhibited a slight tail, which could be a result of some irreversibly terminated macroinitiators. Similar tails have been previously reported for methacrylate-rich copolymers by NMP.[50] However, the majority of the chains appeared to be growing steadily, resulting in a block copolymer with two distinct segments. The addition of the second block was also characterized by the change in composition from the macroinitiator to the final block copolymer (Table 5). For example, the macroinitiator OM80/20 had a composition $F_{VBK} < 0.01$, $F_{MEO2MA} = 0.24$ and $F_{OEGMA8\text{-}9} = 0.76$. After being used to reinitiate a MEO_2MA-rich ternary mixture, the final OM80/20-OM20/80 block copolymer had an overall composition of $F_{MEO2MA} = 0.38$ and $F_{OEGMA8\text{-}9} = 0.60$. These results indicate that poly(VBK-*ran*-MEO_2MA-*ran*-

$OEGMA_{8-9}$) terpolymers synthesized by NMP were pseudo-"living" enough to re-initiate a second ternary batch of monomers to make block copolymers where each of the blocks had distinct MEO_2MA:OEGMA compositions.

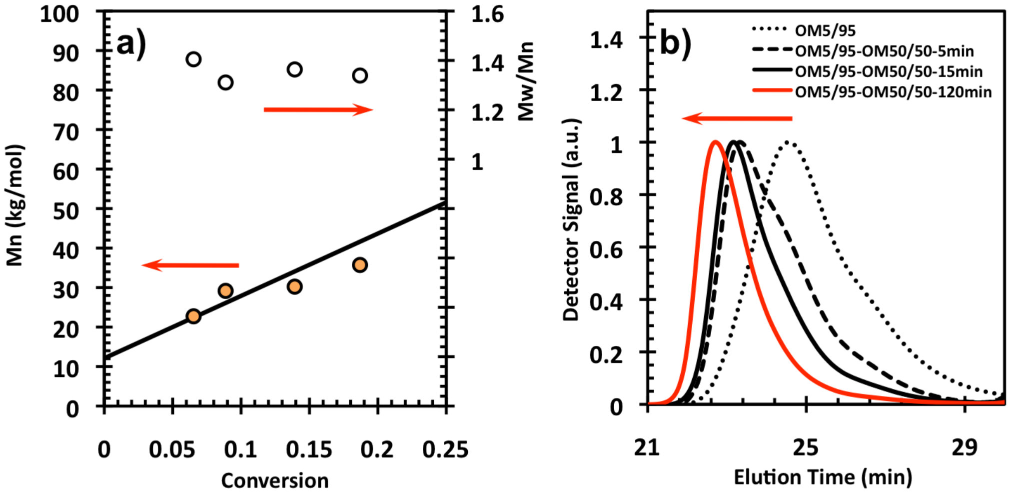


Figure 4. Characteristic a) $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ versus conversion and b) gel permeation chromatograms for chain extension from an OM5/95 macroinitiator using a second batch of 2-(2-methoxyethoxy)ethyl methacrylate/oligo(ethylene glycol) methyl ether methacrylate/9-(4-vinylbenzyl)-9H-carbazole (MEO_2MA/$OEGMA_{8-9}$/VBK). The feed compositions for the second batches of monomer are listed in Table 2. The molecular characteristics of the final block copolymers are summarized in Table 5.

Terpolymer Solution Properties

The final $OEGMA_{8-9}$/VBK and MEO_2MA/VBK copolymers were mixed with neutral water (purified by reverse osmosis) to determine water-solubility. At room temperature, $OEGMA_{8-9}$/VBK copolymers with $F_{VBK} \leq 0.09$ were determined to be water-soluble, while all MEO_2MA/VBK copolymers were determined to be water-insoluble at room temperature, even with VBK compositions as low as 1 mol% (Table 3). These results are expected; the incorporation of a hydrophobic comonomer such as VBK will obviously reduce the water-solubility of the final copolymer. A similar water-solubility range ($F_{VBK} \leq 0.07$) was observed for poly(DMAEMA-*ran*-VBK) copolymers.[18] Due to the relatively short pendant EG chains (2 repeat units), poly(MEO_2MA) exhibits relatively low LCSTs ≈ 28 °C.[31] However, by the inclusion of a hydrophobic comonomer (such as VBK), the LCST drops below room temperature and therefore the resulting poly(MEO_2MA-*ran*-VBK) copolymers were not soluble in neutral water at room temperature (≈ 25 °C). However, poly($OEGMA_{8-9}$)s have longer EG side chains (8-9 repeat units) and are known to exhibit LCSTs ≈ 90 °C[31] and therefore the poly($OEGMA_{8-9}$-*ran*-VBK) copolymers remained completely water-soluble at room temperature up to relatively high VBK contents.

As previously mentioned, copolymers consisting of $OEGMA_{8-9}$ and MEO_2MA can result in water-soluble copolymers, which will exhibit CPTs between 25-90°C, depending on the ratio of $OEGMA_{8-9}$ to MEO_2MA. A series of MEO_2MA/$OEGMA_{8-9}$/VBK terpolymers were synthesized with varying $OEGMA_{8-9}$:MEO_2MA ratios, while maintaining $f_{VBK,0} = 0.02$ (see Table 2 for formulations and Table 5 for characterization). The CPTs of the terpolymers were determined by DLS and UV-Vis spectroscopy. The final terpolymer composition, molecular weight characterization and corresponding CPT for each terpolymer can be found in Table 5. The obtained CPTs for the respective terpolymers increased from 28°C to 81°C as the ratio of $OEGMA_{8-9}$:MEO_2MA increased (Table 5). Characteristic DLS and UV-Vis spectra are shown in Figure 5a and Figure 5b. The resulting CPTs determined by DLS and UV-Vis for each terpolymer exhibited LCST differences of about 0-4 °C, depending on the technique used. Similar slight discrepancies have been observed in our previous work using DMAEMA/VBK copolymers and block copolymers, and is a result of the differences in detection methods.[18] The UV-Vis spectra (Figure 5b) indicate a completely thermo-reversible transition with a slight hysteresis of 1-3 °C between the heating and cooling cycle of each copolymer. Similar "tunability" of copolymer LCSTs in aqueous solutions with identical concentration (3 g·L^{-1}), have previously been obtained using poly(OEGMA$_{8-9}$-*ran*-MEO$_2$MA) copolymers synthesized by ATRP.[31] Just like the copolymers made by ATRP, NMP can be used to synthesize a library of well-defined OEGMA$_{8-9}$/MEO$_2$MA copolymers in a controlled manner, which have a tunable LCST, except that additional functionality was imparted by using a small amount of VBK as the "controlling" comonomer in the BlocBuilder-mediated NMP.

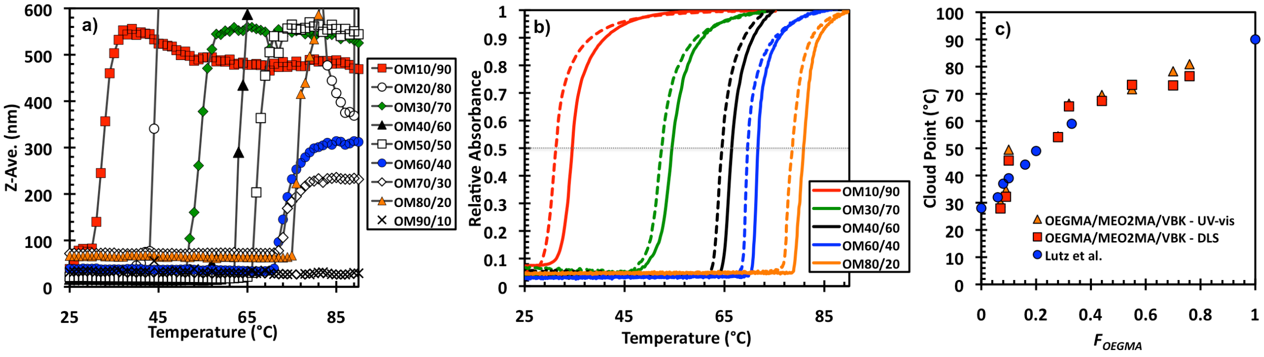


Figure 5. Cloud point temperature (CPT) determined by a) dynamic light scattering (DLS) and by b) UV-Vis spectroscopy of characteristic poly(OEGMA$_{8-9}$-*ran*-MEO$_2$MA-*ran*-VBK) terpolymers (see Table 5 for complete characterization and identification of samples) in neutral water (pH = 7). CPTs were determined using 3 g·L^{-1} solutions. The dotted lines in b) represent the relative absorbance during the cooling process. As a comparison, the resulting CPTs obtained using DLS and UV-Vis in Figure 5a) and 5b) are plotted as a function of F_{OEGMA} in c) along with the corresponding literature values for poly(OEGMA$_{8-9}$-*ran*-MEO$_2$MA) binary copolymers obtained from Lutz. et al.[31]

Block Co(terpolymer) Solution Properties

The final poly(MEO_2MA-*ran*-$OEGMA_{8-9}$-*ran*-VBK)-*block*-poly(MEO_2MA-*ran*-$OEGMA_{8-9}$-*ran*-VBK) block copolymers synthesized by chain extension from MEO_2MA/$OEGMA_{8-9}$/VBK terpolymers were also investigated, to determine their potential for thermo-responsive behavior with multiple LCSTs. The characteristic DLS and UV-Vis spectra are shown in Figure 6. Due to the distinct segments of the block copolymer which possess different $OEGMA_{8-9}$:MEO_2MA ratios (see Table 5 for characterization data), the final block copolymer exhibited two distinct CPTs (Figure 6 and Figure 7). For example OM10/90-OM50/50 exhibited a CPT characterized by a sudden increase in particle size ($Z_{AVG} \approx 400$ nm) at T = 39.2 °C corresponding to the OM10/90 segment and a second CPT corresponding to a second increase in particle size ($Z_{AVG} > 800$ nm) at T = 53.8°C corresponding to the OM50/50 segment (Figure 6b). The mean count of the particles was also plotted (Figure 6e) and shows good agreement with the transitions observed by tracking the change in Z_{AVG}. The first CPT (corresponding to OM10/90) in the block copolymer is slightly higher (CPT = 39.2 °C by DLS) than the CPT previously determined for the OM10/90 macroinitiator (CPT = 32.2 °C by DLS – Table 5). This increase in CPT is due to the addition of a second more water-soluble block (below the second CPT as the second block was more water-soluble). The hydrophilic block improves the hydration of the responsive block and, due to the entropy-driven nature of the phase separation, leads to a higher CPT. Kotsuchibashi et al. reported micelle formation for poly(NIPAAm)-*block*-poly(NIPAAm-co-N-(isobutoxymethyl)acrylamide) block copolymers when heating between the two corresponding LCSTs.[21] Similar observations have also been reported between poly(DMAEMA-*ran*-VBK) and poly(DMAEMA-*ran*-VBK)-*block*-poly(*N,N*-dimethylacrylamide) as the addition of the water-soluble poly(*N,N*-dimethylacrylamide) segment resulted in an increase in LCST and the formation of micelles above the LCST.[18] The second CPT observed for OM10/90-OM50/50 at T = 53.8°C was a result of the chain extension that was formulated to mimic the OM50/50 terpolymer (segment OM50/50), which was previously determined to have an CPT = 67.4 °C. Using a similar reasoning as above, the second block of thermo-responsive terpolymer was now coupled to a water-insoluble segment (when the temperature is above the first CPT but below the second CPT) and now less energy was required to render the entire block copolymer insoluble, hence resulting in a decrease in the second CPT for the OM50/50 block of the block copolymer. Similarly, OM80/20-OM20/80 exhibited a CPT characterized by a sudden increase in particle size ($Z_{AVG} \approx 500$ nm) at T = 40.8 °C corresponding to the OM20/80 segment (assuming the composition used in the formulation results in a segment with similar final composition as the OM20/80 terpolymer previously synthesized) and a second CPT corresponding to a second increase in particle size ($Z_{AVG} > 2000$ nm) at T = 72.4 °C corresponding to the OM80/20 segment, which was the macroinitiator used for the chain extension (see Table 2 for the formulation and Table 5 for characterization data and Figure 6 for the transitions). Similar to OM10/90-OM50/50, the first CPT for OM80/20-OM20/80 is slightly higher than the obtained CPT value for the corresponding OM80/20 terpolymer and the second CPT is slightly lower than the CPT previously determined for the OM20/80 macroinitiator (Table 5 and Figure 6). The corresponding UV-Vis spectra can also be found in Figure 6g) for OM5/95-OM50/50, Figure 6h) for OM10/90-OM50/50 and Figure 6i) for OM80/20-OM20/80 and provide evidence of dual responsiveness of the block copolymers, in good agreement with the data obtained using DLS (see Table 5 for CPTs and Figure 6). As an example, Figure 7 displays visually the double thermo-responsive behaviour of OM10/90-OM50/50. The UV-Vis spectra in Figure 6g)-i) also indicate that the thermo-responsive behavior is again completely reversible, even for the block copolymers, resulting in only a slight hysteresis of 1-4 °C between the heating and cooling cycles.

The properties described in Figure 5 and Figure 6 illustrates the power of compositional and microstructural control imparted by NMP into essentially pure $MEO_2MA/OEGMA_{8-9}$ copolymers (with a minimal amount of VBK). These dual thermo-responsive materials could potentially be used in the fabrication of multi-level sensors or more complex drug delivery vehicles, without using multiple functional monomers, but rather just by modifying the composition of $OEGMA_{8-9}$ relative to MEO_2MA in the respective blocks.

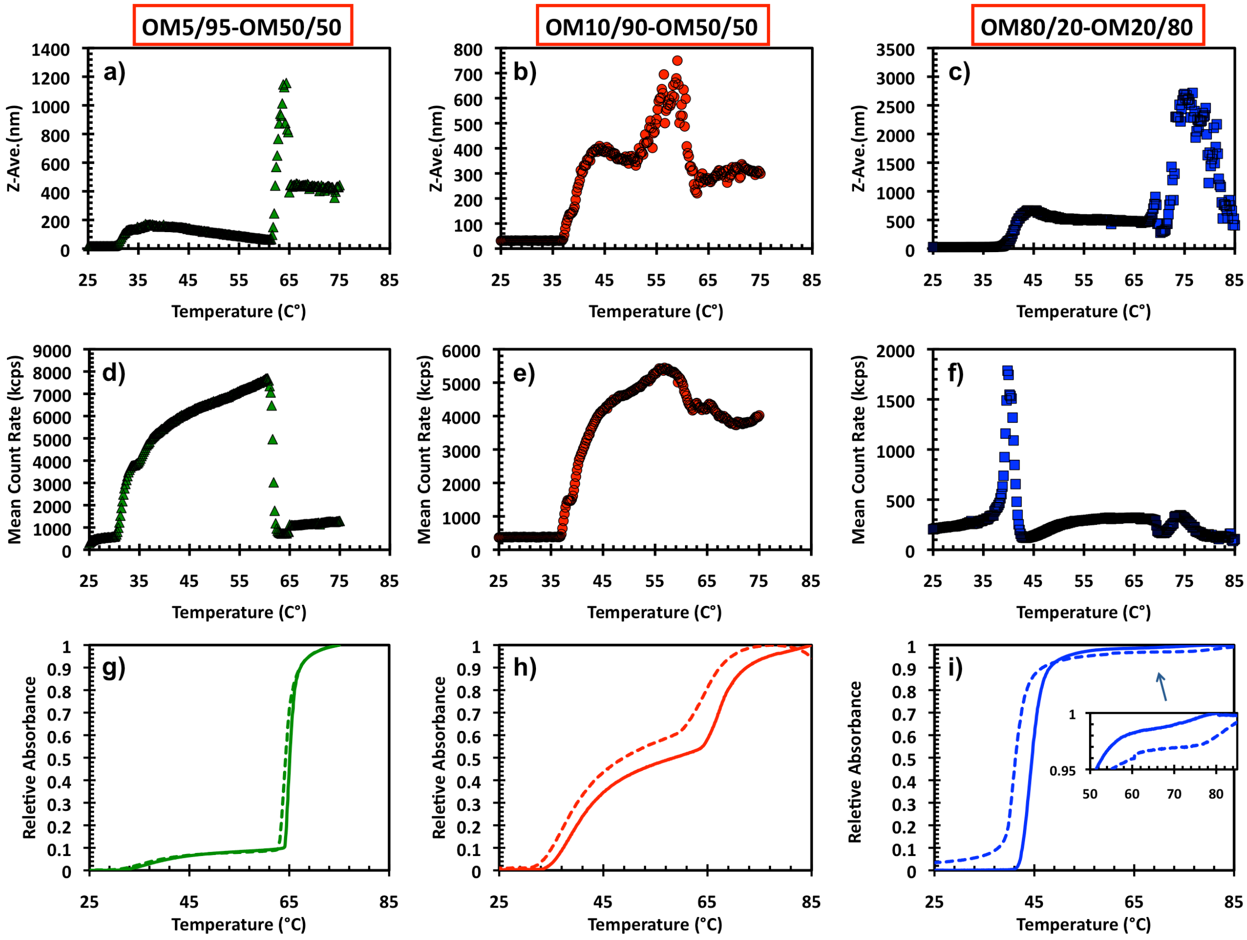


Figure 6. Dual cloud point temperature (CPT) determination by dynamic light scattering (DLS), where a), b) and c) represent the Z-average diameter with respect to temperature and d, e) and f)

represent the mean count rate for OM5/95-OM50/50, OM10/90-OM50/50 and OM80/20-OM20/80 block copolymers, respectively. The corresponding temperature modulated UV-Vis spectra for g) OM5/95-OM50/50, h) OM10/90-OM50/50 and i) OM80/20-OM20/80 block copolymers are also represented. The inset in i) represents a close-up of the upper region of the spectrum. The molecular characteristics of the final block copolymers along with the respective CPTs can be found in Table 5. CPTs were determined using 3 g·L^{-1} solutions in all cases.

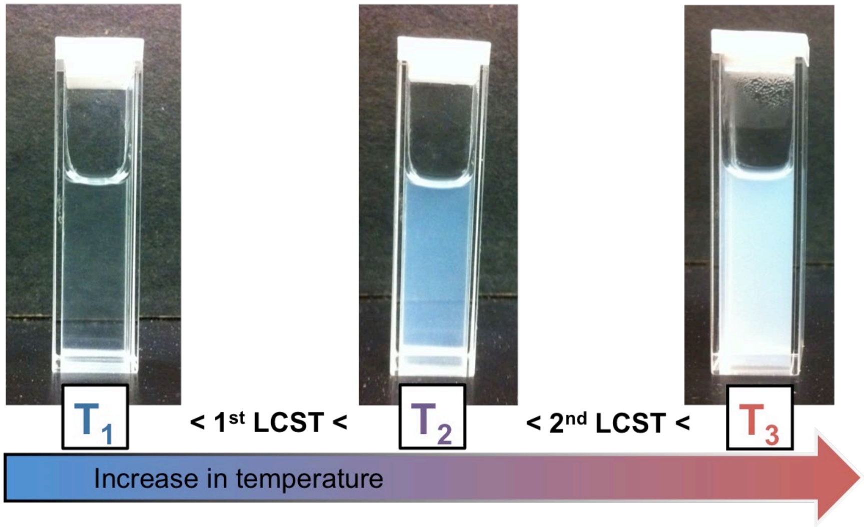


Figure 7. Visual observation of dual cloud point temperature (CPT) is shown for a sample heated to three temperatures bracketing the CPTs of the corresponding block copolymers where each block has different $MEO_2MA/OEGMA_{8-9}$ ratios. In this example, a 3 g·L^{-1} solution of OM10/90-OM50/50 is depicted at various temperatures. The solution is water-soluble at T_1 (room temperature) but becomes translucent as it is heated to T_2 while above the second CPT at T_3, the solution turned milky. The molecular characteristics of the final block copolymers along with the respective CPTs can be found in Table 5.

Terpolymer Fluorescence

In addition to "controlling" the polymerization of MEO_2MA and $OEGMA_{8-9}$, the VBK unit introduces hole transport and fluorescence properties into the final copolymer due to the carbazole moiety. The fluorescence spectra of the terpolymers OM50/50 and OM10/90, when excited at λ = 330 nm, exhibit two major emission peaks at 350 nm and 366 nm, corresponding to the carbazole group in the VBK unit (Figure 8).[18,63] As the temperature increases, the corresponding fluorescence intensity decreases (Figure 8). Similar increases in fluorescence quenching was previously reported for poly(DMAEMA-*ran*-VBK) copolymers.[18] The decrease in intensity appears to be constant over the temperature range of 25 °C to 65 °C with no apparent "step" or change in rate of fluorescence quenching with respect to the corresponding LCSTs (LCST for OM10/90 ≈ 32-35 °C and LCST for OM50/50 ≈ 67-70 °C). Regardless, the incorporation of as little as 1-2 mol% of VBK into the final terpolymer resulted in a significant fluorescence response throughout a large temperature range, even with solutions as dilute as 3 $mg\cdot L^{-1}$.

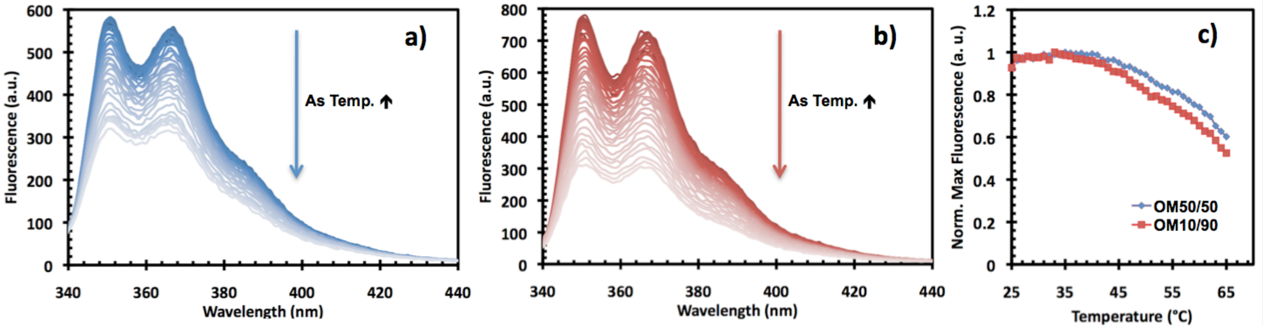


Figure 8. Temperature modulated fluorescence spectra for a) OM50/50 and b) OM10/90. In c), the normalized maximum fluorescence is shown with respect to temperature for both OM50/50 and OM10/90. Fluorescence measurements were determined from 3 $mg\cdot L^{-1}$ solutions using an excitation wavelength of 330 nm at various temperatures.

Conclusion

A series of MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymers were synthesized in a controlled manner by NMP using BlocBuilder/SG1 at 80 °C. The binary copolymerizations exhibited linear increases in $\overline{M_n}$ versus X, up to $X \approx 0.60$ while maintaining relatively narrow molecular weight distributions with $\overline{M_w}/\overline{M_n} < 1.4$ when using $f_{VBK,0} > 0.01$ (and $\overline{M_w}/\overline{M_n} < 1.6$ when using $f_{VBK,0} = 0.01$). The experimentally obtained $<k_P><K>$ values for the MEO_2MA/VBK and $OEGMA_{8-9}$/VBK copolymerizations were similar to each other and were approximately 2 times less than reported $<k_P><K>$ values for MMA/VBK and DMAEMA/VBK copolymerizations performed at similar conditions. The binary copolymer composition, in the studied compositional range, was also similar to that of MMA/VBK copolymerizations, indicating a preferential addition of VBK to itself relative to the respective methacrylate. MEO_2MA/$OEGMA_{8-9}$/VBK terpolymerizations with fixed VBK controller content and various MEO_2MA:$OEGMA_{8-9}$ ratios, resulted in controlled polymerizations and narrow molecular weight distributions (in most cases: $\overline{M_w}/\overline{M_n} < 1.3$). Depending on the final relative MEO_2MA:$OEGMA_{8-9}$ composition, the terpolymers exhibited various CPTs between ~ 28 - 81 °C. Therefore, by tuning the composition, it is possible to tune the LCST of the resulting terpolymer. Finally, characteristic terpolymers were used to initiate a second terpolymerization of MEO_2MA/$OEGMA_{8-9}$/VBK, giving rise to block copolymers consisting of two distinct blocks characterized by different compositions of MEO_2MA to $OEGMA_{8-9}$. The block copolymers exhibited dual CPTs corresponding to each terpolymer segment. In summary, NMP permitted the synthesis of block copolymers where each block had a distinct MEO_2MA:$OEGMA_{8-9}$ composition, that yielded specific, tunable CPTs for each block between ~28 - 81 °C. The inclusion of VBK as the "controlling" BlocBuilder-mediated monomer not only allowed the synthesis of such materials in a controlled fashion but also introduced thermo-responsive fluorescence into the final block copolymers.

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Table 1 Experimental Formulations for 2-(2-Methoxyethoxy)Ethyl Methacryate (MEO_2MA)/9-(4-Vinylbenzyl)-9H-Carbazole (VBK) and Oligo(ethylene glycol) methyl ether methacrylates ($OEGMA_{8-9}$)/VBK Random Binary Copolymerizations Performed at 80°C in a 50 wt% *N,N*-Dimethylformamide (DMF) Solution.

Exp. ID[a]	$[BB]_0$ [b] (mol L^{-1})	$[SG1]_0$ (mol L^{-1})	$[VBK]_0$ (mol L^{-1})	$[MEO_2MA]_0$ (mol L^{-1})	$[OEGMA_{8-9}]_0$ (mol L^{-1})	$[DMF]_0$ (mol L^{-1})	$f_{VBK,0}$ [c]
MEO_2MA/VBK-1	0.0115	0.0011	0.02	1.51	0	9.36	0.01
MEO_2MA/VBK-5	0.0121	0.0012	0.08	1.49	0	9.76	0.05
MEO_2MA/VBK-10	0.0121	0.0012	0.15	1.38	0	9.68	0.10
MEO_2MA/VBK-20	0.0074	0.0007	0.18	0.72	0	5.95	0.20
$OEGMA_{8-9}$/VBK-1	0.0124	0.0013	0.01	0	0.68	9.90	0.01
$OEGMA_{8-9}$/VBK-5	0.0122	0.0012	0.03	0	0.66	9.99	0.05
$OEGMA_{8-9}$/VBK-10	0.0123	0.0012	0.07	0	0.64	9.84	0.10
$OEGMA_{8-9}$/VBK-20	0.0123	0.0013	0.15	0	0.59	9.92	0.20

[a] Experimental identification (Exp. ID) for OEGMA with VBK and MEO_2MA with VBK copolymerizations are given by VBK/OEGMA -Y and VBK/ MEO_2MA -Y, respectively, with VBK representing 9-(4-vinylbenzyl)-9H-carbazole, OEGMA representing Oligo(ethylene glycol) methyl ether methacrylate, MEO_2MA representing 2-(2-methoxyethoxy)ethyl methacrylate and Y representing the initial mol % of VBK in the feed. All copolymerizations were done in 50 wt % DMF solution with target average molecular weight of approximately 25 kg·mol $^{-1}$ while using an initial molar ratio of SG1 relative to BlocBuidler = $r = [SG1]_0 / [BB]_0 = 0.1$.

[c] $f_{VBK,0}$ is the initial molar fraction of VBK in the feed.

Table 2 Experimental Formulation for Various Oligo(ethylene glycol) methyl ether methacrylates /2-(2-Methoxyethoxy)Ethyl Methacryate /9-(4-Vinylbenzyl)-9H-Carbazole (OEGMA$_{8-9}$/MEO$_2$MA/VBK) Random Terpolymerizations and Chain Extensions Performed at 80°C in a 50 wt% *N,N*-Dimethylformamide (DMF) Solution.

Exp. ID [a]	$[BB]_0$ [b] (mmol L^{-1})	$[SG1]_0$ (mmol L^{-1})	$[VBK]_0$ (mol L^{-1})	$[MEO_2MA]_0$ (mol L^{-1})	$[OEGMA_{8-9}]_0$ (mol L^{-1})	$f_{VBK,0}/f_{MEO2MA,0}$ [c]	$\overline{M}_n^{Target}$
OM5/95	15.62	1.69	0.037	1.85	0.10	0.02 / 0.94	25.7
OM10/90	12.92	1.30	0.037	1.66	0.17	0.02 / 0.89	30.7
OM20/80	9.50	0.93	0.031	1.23	0.30	0.02 / 0.79	39.2
OM30/70	7.94	0.83	0.029	1.02	0.42	0.02 / 0.69	49.0
OM40/60	6.28	0.63	0.026	0.79	0.52	0.02 / 0.59	61.9
OM50/50	4.66	0.57	0.024	0.59	0.59	0.02 / 0.49	82.0
OM60/40	3.45	0.38	0.022	0.44	0.65	0.02 / 0.40	110.6
OM70/30	2.58	0.29	0.002	0.32	0.74	0.02 / 0.30	153.0
OM80/20	1.66	0.21	0.020	0.19	0.80	0.02 / 0.19	242.0
OM90/10	0.85	0.10	0.019	0.09	0.84	0.02 / 0.10	472.5

Exp. ID [a]	$[Macro.]_0$ (mmol L^{-1})	$[VBK]_0$ (mol L^{-1})	$[MEO_2MA]_0$ (mol L^{-1})	$[OEGMA_{8-9}]_0$ (mol L^{-1})	$f_{VBK,0}/f_{MEO2MA,0}$ [c]	$\overline{M}_n^{Target}$
OM5/95-OM50/50	2.29	0.031	0.66	0.63	0.02 / 0.50	181.6
OM10/90-OM50/50	0.79	0.026	0.66	0.63	0.02 / 0.50	522.5
OM80/20-OM20/80	0.65	0.037	0.96	0.22	0.02 / 0.79	211.4

[a] Experimental identification (Exp. ID) for OEGMA$_{8-9}$, MEO$_2$MA and VBK terpolymerizations are given by OMX/Y, with “O” representing oligo(ethylene glycol) methyl ether methacrylate, “D”

representing 2-(2-methoxyethoxy)ethyl methacrylate and X/Y representing the respective, initial mol % of $OEGMA_{8-9}$:MEO_2MA in the feed. For the chain extensions, the Exp. ID is given by OMX/Y- OMZ/W where OMX/Y represents the Exp. ID of the macroinitiator used for the chain extension and for OMZ/W, the “O” represents oligo(ethylene glycol) methyl ether methacrylate, “M” representing 2-(2-methoxyethoxy)ethyl methacrylateand Z/W representing the approximate initial mol % of $OEGMA_{8-9}$:MEO_2MA in the feed, respectively. All polymerizations were done in 50 wt % DMF solution, in the case of the terpolymerizations the $[DMF]_0 = 8.2$ mol L^{-1} and in the case of the chain extensions $[DMF]_0 = 13.0$ mol L^{-1}.

[b] $[BB]_0$ represents the initial concentration of BlocBuilder initiator.

[c] $f_{VBK,0}$ and $f_{MEO2MA,0}$ are the respective initial molar fractions of VBK and MEO_2MA in the feed.

Table 3 Molecular Characterization for 2-(2-Methoxyethoxy)Ethyl Methacryate (MEO_2MA)/9-(4-Vinylbenzyl)-9H-Carbazole (VBK) and Oligo(ethylene glycol) methyl ether methacrylates ($OEGMA_{8-9}$)/VBK Random Binary Copolymers Synthesized at 80°C in a 50 wt% *N,N*-Dimethylformamide (DMF) Solution

Exp. ID [a]	X^b	$t_{polym.}$ (min)	$\overline{M_n}^b$ (kg/mol)	$\overline{M_w}/\overline{M_n}^b$	F_{VBK} [d]	F_{MEO2MA} [d]	$F_{OEGMA8-9}$ [d]	Water Soluble [e]
MEO_2MA/VBK-1	0.48	216	14.7	1.64	<0.01	>0.99	0	No
MEO_2MA/VBK-5	0.49	313	12.1	1.34	0.08	0.92	0	No
MEO_2MA/VBK-10	0.42	355	9.6	1.24	0.16	0.84	0	No
MEO_2MA/VBK-20	0.21	424	7.1	1.19	0.36	0.64	0	No
$OEGMA_{8-9}$/VBK-1	0.50	189	12.6	1.28	<0.01	0	>0.99	Yes
$OEGMA_{8-9}$/VBK-5	0.50	286	11.2	1.28	0.09	0	0.91	Yes
$OEGMA_{8-9}$/VBK-10	0.27	386	8.3	1.19	0.27	0	0.73	No
$OEGMA_{8-9}$/VBK-20	0.23	368	5.0	1.11	0.27	0	0.73	No

[a] Experimental identification (Exp. ID) for OEGMA with VBK and MEO_2MA with VBK copolymerizations are given by VBK/OEGMA -Y and VBK/ MEO_2MA -Y, respectively, with VBK representing 9-(4-vinylbenzyl)-9H-carbazole, OEGMA representing Oligo(ethylene glycol) methyl ether methacrylate, MEO_2MA representing 2-(2-methoxyethoxy)ethyl methacrylate and Y representing the initial mol % of VBK in the feed. All copolymerizations were done in 50 wt % DMF solution with target average molecular weight of 25 kg·mol $^{-1}$.

[b] monomer conversion, as determined by ^{1}H NMR spectroscopy.

[c] Number average molecular weight ($\overline{M_n}$) and polydispersity index ($\overline{M_w}/\overline{M_n}$) were determined using gel permeation chromatography (GPC) run in THF at 35°C and calibrated against poly(styrene) standards

[d] F_{VBK}, F_{MEO2MA}, and $F_{OEGMA8-9}$ are the final molar composition of VBK, MEO_2MA and $OEGMA_{8-9}$ in the copolymer, as determined by ^1H NMR spectroscopy.

[e] Water-solubility of the final polymer was checked in neutral pH solution at room temperature.

Table 4 Experimentally Derived Kinetic Parameters for 2-(2-Methoxyethoxy)Ethyl Methacryate (MEO_2MA)/9-(4-Vinylbenzyl)-9H-Carbazole (VBK) and Oligo(ethylene glycol) methyl ether methacrylates ($OEGMA_{8-9}$)/VBK Copolymerizations Done at 80°C in 50 wt% *N,N*-Dimethylformamide (DMF) Solutions.

Exp. ID[a]	r [b]	$f_{VBK,0}$ [c]	$<k_P>[P\cdot]$[c] (s^{-1})	$<k_P><K>$[c] (s^{-1})
MEO_2MA/VBK-1	0.10	0.01	$(2.9 \pm 0.2) \times 10^{-5}$	$(2.8 \pm 0.2) \times 10^{-6}$
MEO_2MA/VBK-5	0.10	0.05	$(3.0 \pm 0.2) \times 10^{-5}$	$(3.1 \pm 0.2) \times 10^{-6}$
MEO_2MA/VBK-10	0.10	0.10	$(1.5 \pm 0.3) \times 10^{-5}$	$(1.6 \pm 0.3) \times 10^{-6}$
MEO_2MA/VBK-20	0.10	0.20	$(9.1 \pm 1.5) \times 10^{-6}$	$(9.1 \pm 1.5) \times 10^{-7}$
$OEGMA_{8-9}$/VBK-1	0.10	0.01	$(2.8 \pm 0.6) \times 10^{-5}$	$(2.9 \pm 0.7) \times 10^{-6}$
$OEGMA_{8-9}$/VBK-5	0.10	0.05	$(2.9 \pm 0.5) \times 10^{-5}$	$(2.8 \pm 0.5) \times 10^{-6}$
$OEGMA_{8-9}$/VBK-10	0.10	0.10	$(1.0 \pm 0.1) \times 10^{-5}$	$(1.0 \pm 0.1) \times 10^{-6}$
$OEGMA_{8-9}$/VBK-20	0.11	0.20	$(8.5 \pm 0.8) \times 10^{-6}$	$(9.1 \pm 0.8) \times 10^{-7}$

[a] Experimental identification (Exp. ID) for OEGMA with VBK and MEO_2MA with VBK copolymerizations are given by VBK/OEGMA-Y and VBK/ MEO_2MA-Y, respectively, with VBK representing 9-(4-vinylbenzyl)-9H-carbazole, OEGMA representing Oligo(ethylene glycol) methyl ether methacrylate, MEO_2MA representing 2-(2-methoxyethoxy)ethyl methacrylate and Y representing the initial mol % of VBK in the feed. All copolymerizations were done in 50 wt % DMF solution with target average molecular weight of 25 kg·mol $^{-1}$.

[b] Initial molar ratio of SG1 free nitroxide to BlocBuilder alkoxyamine used in the copolymerization: $r = [\mathrm{SG1}]_0/[\mathrm{BlocBuilder}]_0$

[c] Product of the average propagation rate constant, $<k_P>$, and the average equilibrium constant, $<K>$. Error derived from standard error in slope of scaled conversion ($\ln(1-X)^{-1}$) versus time plots.

Table 5 Molecular Characterization for Various Oligo(ethylene glycol) methyl ether methacrylates /2-(2-Methoxyethoxy)Ethyl Methacryate /9-(4-Vinylbenzyl)-9H-Carbazole (OEGMA$_{8-9}$/MEO$_2$MA/VBK) Random Terpolymers and Block Copolymers.

Exp. ID [a]	$\overline{M_n}$ (kg/mol) [b]	$\overline{M_w}/\overline{M_n}$ [b]	F_{VBK} [c]	F_{MEO2MA} [c]	$F_{OEGMA8-9}$ [c]	CPT [d] (°C) DLS (UV)
OM5/95	12.0	1.58	<0.01	0.93	0.07	27.9 (30.1)
OM10/90	18.5	1.55	0.02	0.88	0.09	32.2 (34.6)
OM20/80	23.1	1.28	<0.01	0.90	0.10	45.5 (49.5)
OM30/70	23.4	1.28	0.02	0.70	0.28	54.1 (54.4)
OM40/60	28.7	1.34	<0.01	0.68	0.32	65.4 (66.4)
OM50/50	35.9	1.28	0.03	0.53	0.44	67.4 (69.6)
OM60/40	22.9	1.38	0.03	0.41	0.55	73.3 (71.7)
OM70/30	43.2	1.22	0.05	0.25	0.70	73.1 (78.3)
OM80/20	39.2	1.20	<0.01	0.24	0.76	76.5 (80.9)
OM90/10	47.7	1.27	<0.01	0.02	0.98	>90*(>90)*

Exp. ID [a]	$\overline{M_n}$ (kg/mol) [b]	$\overline{M_w}/\overline{M_n}$ [b]	F_{VBK} [c]	F_{MEO2MA} [c]	$F_{OEGMA8-9}$ [c]	1st CPT / 2nd CPT [d] (°C) DLS$_1$ (UV)$_1$ / DLS$_2$ (UV)$_2$
OM5/95-OM50/50	39.6	1.30	<0.01	0.51	0.49	31.2(39.3) / 62.4(65.1)
OM10/90-OM50/50	35.2	1.69	0.04	0.91	0.05	39.2(41.2) / 53.8(67.8)
OM80/20-OM20/80	91.9	1.95	0.02	0.38	0.60	40.8(44.5) / 72.4(72.8)

[a] Experimental identification (Exp. ID) for OEGMA$_{8-9}$, MEO$_2$MA and VBK terpolymerizations are given by OMX/Y, with "O" representing oligo(ethylene glycol) methyl ether methacrylate, "M" representing 2-(2-methoxyethoxy)ethyl methacrylate and X/Y representing the approximate initial

mol % of $OEGMA_{8-9}/MEO_2MA$ in the feed, respectively. For the chain extensions, the Exp. ID is given by OMX/Y- OMZ/W where OMX/Y represents the Exp. ID of the macroinitiator used for the chain extension and for OMZ/W, the “O” represents oligo(ethylene glycol) methyl ether methacrylate, “M” represents 2-(2-methoxyethoxy)ethyl methacrylate and Z/W represents the approximate initial mol % of $OEGMA_{8-9}/MEO_2MA$ in the feed, respectively.

[b] Number average molecular weight ($\overline{M_n}$) and polydispersity index ($\overline{M_w}/\overline{M_n}$) were determined using gel permeation chromatography (GPC) run in THF at 35 °C and calibrated against poly(styrene) standards.

[c] F_{VBK}, F_{MEO2MA} and $F_{OEGMA8-9}$ are the final molar composition of VBK, MEO_2MA and $OEGMA_{8-9}$ in the copolymer, as determined by ^1H NMR spectroscopy.

[d] Cloud point temperature (CPT) was determined by dynamic light scattering (DLS) and UV-Vis spectroscopy (UV/Vis) for a 3 $g \cdot L^{-1}$ polymer and water solution.

*No CPT was observed between 20 and 90 °C.

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