Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(methacrylate-*ran*-styrene) Block Copolymers with Tunable Mechanical Properties by Nitroxide Mediated Controlled Radical Polymerization

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Abstract: Poly(styrene-*alt*-maleic anhydride)-*block*-poly(methacrylate-*ran*-styrene) block copolymers were synthesized from low dispersity (M_w/M_n=1.24) and perfectly alternating poly(styrene-*alt*-maleic anhydride) macroinitiators, by nitroxide mediated controlled radical polymerization (NMP), using various methacrylate-rich mixtures: methyl methacrylate/styrene (MMA/S), ethyl methacrylate/styrene (EMMA/S), *n*-butyl methacrylate/styrene (BMA/S) and benzyl methacrylate/styrene (BzMA/S). Some irreversible termination was present during the chain extension from the macroinitiator, resulting in some bimodality in the molecular weight distribution of the final block copolymer ($\approx$2% to $\approx$25% dead chains) which is common for methacrylate/styrene copolymerizations by NMP. The resulting final block copolymers were determined to be methacrylate-rich (molar ratio XMA/S $\approx$3.3 to 5.5) by ^{1}H NMR and the resulting glass transition temperature (T_g) of the chain-extended segments were found to be similar to the corresponding pure poly(methacrylate)s. NMP allows the controlled placement of functional maleic anhydride containing segments within a block copolymer with tunable mechanical properties by simple substitution of methacrylate monomer used in synthesis.

Keywords: nitroxide mediated controlled radical polymerization (NMP), maleic anhydride (MA), methacrylate, alternating copolymer, block copolymer.

Introduction

Controlled radical polymerization (CRP) has allowed the synthesis of complex microstructured materials with relative ease compared to more traditional "living" techniques such as ionic polymerization.[1,2] Among numerous CRP techniques, the most popular are atom transfer radical polymerization (ATRP),[3,4] nitroxide mediated polymerization (NMP),[5-7] and reversible addition-fragmentiation chain transfer polymerization (RAFT).[8,9] Traditional first generation NMP initiators such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) were generally restricted to the polymerization of styrenics due to TEMPO's elevated activation temperature (>125 °C).[10,11] Second-generation NMP alkoxyamine initiators based on *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1) have allowed the synthesis of poly(acrylates),[12-15] poly(acrylamides),[16-18] and even poly(methacrylates) when using the comonomer approach.[19-23] In addition to incorporating more complex monomers, SG1 based initiators have permitted synthesis of copolymers with controlled microstructures. Maleic anhydride (MA) is not easily homopolymerized,[24] however, under the appropriate conditions a mixture of styrene and MA is known to produce alternating copolymers.[25] Recently, our group has reported the one-pot synthesis of perfectly alternating poly(styrene-*alt*-maleic anhydride) copolymers as well as poly(styrene-*alt*-maleic anhydride)-*block*-poly(styrene) block copolymers by NMP.[26] We found that to obtain this desired molecular architecture it was required that the copolymerization temperature be kept below 90 °C to reduce the preferential addition of styrene at low conversions over the alternating motif at non-equimolar feed mixtures.[26] Others were also able to target this molecular architecture under proper conditions.[27-29] MA has attracted a lot of attention due to its ability to undergo post-synthesis imidization reactions and to be used in numerous applications such as blend compatibilizers[30-32] or TiO$_2$ nanoparticle anchors.[33] The functional MA containing segments can also be used as "grafting-to" sites and used for applications as a flow improver for oils,[34] drug delivery systems,[35,36] and molecular biosurface engineering.[37] Recently we explored the use of poly(S-*alt*-MA) and poly(S-*alt*-MA)-*block*-poly(S) as templates for the self-assembly of thiophene decorated nanorods and spheres.[38] This study further illustrates the versatility of MA functional polymers and how the controlled

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placement of their MA units can be used to significantly affect material properties and morphologies in bulk or solution.

In this study we expand on the use of perfectly alternating poly(styrene-*alt*-maleic anhydride) macroinitiators to synthesize block copolymers with controlled microstructures and tunable mechanical properties (*e.g.* here we measured the glass transition) (Scheme I). The perfectly alternating copolymer allows controlled placement of the MA reactive sites while the various methacrylates allow for tunable glass transition temperature of the block copolymer. We address first the synthesis and characterization of the block copolymers followed by measurement of the glass transition temperature for the block copolymers with different methacrylates in the second block.

Experimental

Materials. Styrene (≥99%), methyl methacrylate (MMA, ≥98.5%), ethyl methacrylate (EMA, ≥99%), *n*-butyl methacrylate (nBMA, ≥99%), and benzyl methacrylate (BzMA, 96%) were all obtained from Sigma Aldrich and purified by passage through a column containing a mixture of basic alumina and calcium hydride (40:1 weight ratio) and stored in a freezer under a head of nitrogen until required. Tetrahydrofuran (THF, ≥99%), 1,4-dioxane (≥99.0%) and hexanes (≥98.5%) were obtained from Fisher Scientific and used as received. The perfectly alternating poly(styrene-*ran*-maleic anhydride) macroinitiator (PSMA) was polymerized according to the literature.[26] These PSMA macroinitiators were synthesized to low conversion, to preserve chain-end fidelity (*i.e.* "livingness"), in accordance to the literature.[26,39]

Synthesis of Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(styrene) (PSMA-PS). The synthesis was done in a 50 mL three-neck round bottom flask with a magnetic Teflon stir bar connected to a condenser that was chilled with cooling water (5 °C). A thermocouple, inserted into a thermowell joined to the reactor, was connected to a temperature controller that used a heating mantle to heat the reactor. The PSMA macroinitiator (0.20 g, 0.013 mmol), styrene (7.76 g, 75 mmol) and 1,4-dioxane (10.34 g) were added to the reactor prior to being sealed with a rubber septum. Nitrogen was then used to bubble the mixture for 25 min, removing any dissolved oxygen and to maintain a positive pressure in the reactor. Once sufficiently bubbled, the nitrogen flow was reduced while the needle was raised above the liquid level to allow the system to be purged throughout the reaction. The temperature controller was set to 110 °C and heating at a rate of 10 °C per minute was commenced. After reaching the set temperature, samples were taken periodically and added to excess methanol until precipitation was observed. After 4 h, the polymerization was cooled to room temperature and the reactor contents were precipitated in methanol and dried in a vacuum oven at 60 °C to evaporate any unreacted monomer or solvent that was still present. The final block copolymer (Yield=1.1 g) was characterized by gel permeation chromatography (GPC) (number average mole-
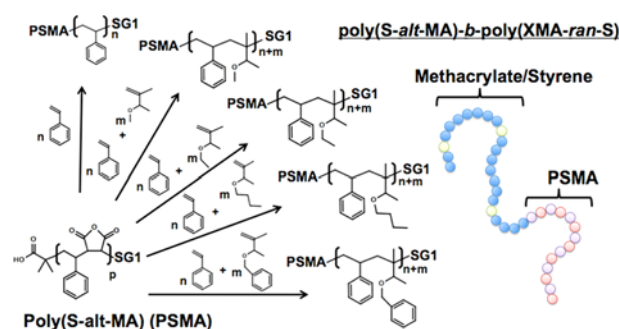
Scheme I. Pure styrene (S) as well as methacrylic monomers such as methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (BMA) and benzyl methacrylate (BzMA) were copolymerized with a small amount of S comonomer (~8-13 mol% S in the feed) by nitroxide-mediated polymerization (NMP) using low dispersity SG1-terminated poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiators to yield block copolymers containing functional maleic anhydride segments along with a methacrylate-rich segment with narrow molecular weight distribution.

cular weight, M_n=74.6 kg·mol^{-1} and polydispersity, M_w/M_n=1.78).

Chain Extension of Various Methacrylate and Styrene Mixtures Using Poly(styrene-*alt*-maleic anhydride) (PSMA) Macroinitiator. The methacrylate/styrene mixture chain extensions from the poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiator were performed with the same experimental set-up as the pure styrene chain extension of PSMA (Scheme I). Various methacrylate/styrene (8-13 mol% styrene relative to methacrylate) mixtures were copolymerized such as methyl methacrylate/styrene (MMA/S), ethyl methacrylate/styrene (EMA/S), *n*-butyl methacrylate/styrene (BMA/S), and benzyl methacrylate/styrene (BzMA/S). All formulations can be found in Table I. As an example, PSMA (0.21 g, 0.014 mmol), EMA (7.33 g, 64 mmol), styrene (0.65 g, 6.3 mmol), and 1,4-dioxane (8.34 g) were added to the reactor, which was then sealed. The reactor was bubbled with nitrogen for 25 min while being stirred. The temperature controller was then set to 90 °C and the nitrogen flow rate reduced. Once the reaction mixture appeared to become more viscous, the mixture was cooled, precipitated in hexanes and dried in the vacuum oven at 60 °C overnight (Yield=12.6%, M_n=299.7 kg·mol^{-1}, M_w/M_n=1.98 and molar ratio of EMA to S, $R_{EMA/S}$=4.2).

Characterization. Molecular weight characterization was determined using gel permeation chromatography (GPC) performed on a Water Breeze GPC. HPLC grade THF was used as the eluent with a flow rate of 0.3 mL·min^{-1}, heated to 40 °C while passing through three Waters Styragel® HR columns connected in series (HR1 with molecular weight measurement range of 10^2-5×10^3 g·mol^{-1}, HR2 with molecular weight measurement range of 5×10^2-2×10^4 g·mol^{-1}, and HR4 with molecular weight measurement range 5×10^3-6×10^5 g·mol^{-1}) and a guard column was used. The GPC was equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors and was calibrated using linear, nearly monodisperse

poly(styrene) standards. The molar ratio of methacrylate relative to styrene of the final samples was determined using ^{1}H NMR spectroscopy which was performed on a 400 MHz Varian Mercury. Characteristic peaks for each monomer were isolated and compared: Styrene (5H, 7.05-7.30 ppm), MMA (3H, 3.76 ppm), EMA (2H, 4.17 ppm), BMA (2H, 4.31 ppm), and BzMA (2H, 5.31 ppm). Glass transition temperatures (T_g) of the block copolymers were determined using differential scanning calorimetry (DSC) Q2000 from TA instruments. The DSC was calibrated for temperature and heat flow using indium and benzoic acid standards, respetively. A heat/cool/heat cycle, with a heat and cool rate of 10 ^{o}C·min^{-1}, was used to eliminate thermal stresses, and the T_g was determined from the midpoint method on the change of slopes in the DSC trace.

Results and Discussion

Block Copolymer Synthesis. Alternating poly(styrene-*alt*-maleic anhydride) (PSMA) copolymers were used as macroinitiators for a fresh batch of styrene as well as various fresh batches of methacrylate/styrene monomer mixtures, namely: methyl methacrylate/styrene (MMA/S), ethyl methacrylate/styrene (EMA/S), *n*-butyl methacrylate/styrene (BMA/S), and benzyl methacrylate/styrene (BzMA/S). All formulations are found in Table I and all final block copolymer molecular weight characterization is found in Table II. The styrene chain extension was done first as it should be an easily controllable monomer by NMP. Figure 1 is the GPC chromatogram for poly(S-*alt*-MA)-*block*-poly(S) (PSMA-PS) and it illustrates a clear monomodal shift from PSMA macroinitiator to the chain-extended PSMA-PS. The chain extension is characterized by a large increase in M_n, from M_n=15.2 to 74.6 kg·mol^{-1} with a slight broadening of the M_w/M_n, from M_w/M_n=1.24 to 1.78. When examining Figure 1 it becomes noticeable that slight tails on either side of the final block copolymer are present. The tail on the leading edge is most likely due to termination by combination resulting in an increase in M_n; while the slight tail on the trailing edge is most likely due to chain transfer to monomer. Chain transfer to monomer is probable due to the relatively high concentration of styrene present in

Table I. Experimental Conditions for Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(styrene) (poly(S-*alt*-MA)-*block*-poly(S)) and Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(x-methacrylate-*ran*-styrene) (poly(S-*alt*-MA)-*block*-poly(XMA-*ran*-S)) Chain Extensions Synthesized in 50 wt% 1,4-Dioxane Solution

Exp. ID[a]	[PSMA]$_0$ (mmol·L^{-1})	[S]$_0$ (mol·L^{-1})	XMA	[XMA]$_0$ (mol·L^{-1})	[dioxane]$_0$ (mol·L^{-1})	Temp (°C)	t_{polym} (h)
PSMA-PS	0.72	4.02	-	0	6.32	110	4.0
PSMA-PMMA/S	0.90	0.42	MMA	5.07	6.08	90	1.2
PSMA-PEMA/S	0.86	0.39	EMA	4.00	5.90	90	1.5
PSMA-PBMA/S	0.86	0.32	BMA	3.37	5.74	90	2.5
PSMA-PBzMA/S	0.87	0.41	BzMA	2.68	5.86	90	1.4

[a]Experimental identification (ID) for the random copolymers is given by PSMA-PX where PSMA corresponds to the poly(styrene-*alt*-maleic anhydride) macroinitiator used in the chain extension and X corresponds to styrene (S), methyl methacrylate and styrene (MMA/S), ethyl methacrylate and styrene (EMA/S), n-butyl methacrylate and styrene (BMA/S) or benzyl methacrylate and styrene (BzMA/S). All experiments were formulated to have $M_{n,target}$=600 kg·mol^{-1}.

Table II. Molecular Characterization for Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(styrene) (poly(S-*alt*-MA)-*block*-poly(S)) and Poly(styrene-*alt*-maleic anhydride)-*block*-Poly(x-methacrylate-*ran*-styrene) (poly(S-*alt*-MA)-*block*-poly(XMA-*ran*-S)) Chain Extensions Synthesized in 50 wt% 1,4-Dioxane Solution

Exp. ID[a]	M_n^b (kg·mol^{-1})	M_w/M_n^b	XMA	$R_{XMA/S}^c$ (mol ratio)	Yeild[d] (%)	T_g^e (°C)
PSMA	15.2	1.23	-	0	-	181.3
PSMA-PS	74.6	1.78	-	0	13.8	102.1
PSMA-PMMA/S	52.6	1.74	MMA	4.6	5.4	118.4
PSMA-PEMA/S	299.7	1.98	EMA	4.2	12.6	77.6
PSMA-PBMA/S	274.0	1.89	BMA	5.5	11.1	33.4
PSMA-PBzMA/S	228.1	2.06	BzMA	3.3	16.4	58.2

[a]Experimental identification (ID) for the random copolymers is given by PSMA-PX where PSMA corresponds to the poly(styrene-*alt*-maleic anhydride) macroinitiator used in the chain extension and X corresponds to styrene (S), methyl methacrylate and styrene (MMA/S), ethyl methacrylate and styrene (EMA/S), n-butyl methacrylate and styrene (BMA/S) or benzyl methacrylate and styrene (BzMA/S). [b]Molecular characteristics of the final copolymer: number average molecular weight (M_n) and weight average molecular weight (MW) determined by GPC using THF as eluent and calibrated using poly(styrene) standards. [c]Final molar ratio between the associated methacrylate (XMA) and styrene (S), determined by ^{1}H NMR spectroscopy. [d]Gravimetric yield of the final block copolymer after precipitation and overnight drying. [e]Glass transition temperature (T_g) determined by midpoint analysis of the second order transition for heat flow versus temperature determined by DSC.
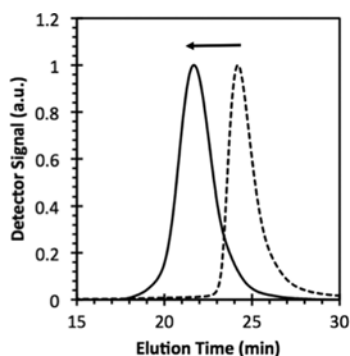
Figure 1. Gel permeation chromatograms (GPC) for styrene chain extension (solid line) from poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiator (dashed line) in 50 wt% 1,4-dioxane at 110 °C. Formulation and characterization data are summarized in Table I and Table II, respectively.

by irreversible termination of the propagating chains or by generation of new chains by initiation of a monomeric radical.[40] Both cases would result in a significant broadening of the molecular weight distribution (higher M_w/M_n).[40] While performing the polymerization to lower conversions and using lower target molecular weights would most likely reduce the termination reactions, the current chain extension proves that the PSMA is "pseudo-living" and can re-initiate a fresh batch of styrene monomer, relatively cleanly, resulting in a final block copolymer with relatively narrow, monomodal molecular weight distributions.

Given the effectiveness of the PSMA macroinitiator at re-initiating cleanly to make chain-extended block copolymer with a second block of poly(styrene), PSMA was also then used to initiate a series of methacrylate/styrene mixtures in order to adjust the mechanical properties (in this case, the T_g was used as the test property) of the second block. All formulations and characterization data are summarized in Table I and Table II, respectively. Similar to the styrene chain extension, Figure 2 illustrates the GPC chromatograms for MMA/S, EMA/S, BMA/S, and BzMA/S chain extensions. In all cases, a clear shift in peak is apparent, characterized by an increase in M_n, from M_n=15.2 kg·mol⁻¹ to 52.6-299.7 kg·mol⁻¹. In all four cases, a peak is present at the same elution time as the PSMA macroinitiator, and this represents premature termination of a portion of the propagating chains.[41,42] While in some cases this second peak represented roughly ≈25% of irreversibly terminated propagating chains (*e.g.* PSMA-MMA/S), some others were much less significant with as little as ≈2% of the chains terminated upon cross-over to the second block (eg. PSMA-EMA/S). The presence of the dead macroinitiator peak is most likely due to loss of initiator efficiency as a result of the high equilibrium constant (K) associated with methacrylates. This high K value means that the growing chains are uncapped or "active" for an extended period of time, increasing the rate of propagation and therefore increasing the probability for
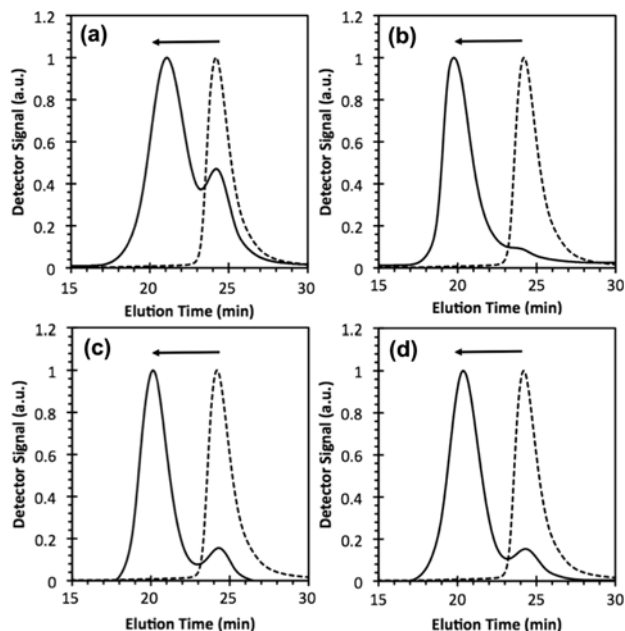

Figure 2. Gel permeation chromatograms (GPC) for X-methacrylate/styrene (XMA/S; X=methyl (M), ethyl (E), *n*-butyl (B) or benzyl (Bz)) chain extensions from poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiator (a) to polymerize MMA/S mixtures, (b) to polymerize EMA/S mixtures, (c) to polymerize BMA/S mixtures, and (d) to polymerize BzMA/S mixtures in 50 wt% 1,4 dioxane at 90 °C. The dotted line represents PSMA macroinitiator while the solid line represents the final methacrylate containing block copolymer. All formulations and characterization data are summarized in Table I and Table II, respectively.

irreversible termination.[43] The "controlling" comonomer in the second batch, styrene in this case, will preferentially become the terminal unit on the propagating chain resulting in a higher propensity for reversible termination, resulting in a controlled polymerization.[41,42] However, once the styrene begins to get consumed and not enough styrene is present, the propagating chain will run a higher risk for irreversible termination.[41,42] Charleux and coworkers observed for MMA/S copolymerizations that a higher $M_{n,experimental}$ compared to $M_{n,theoretical}$ was a result of early termination resulting in initiator inefficiency.[42] Recently, our group observed a similar "second peak" corresponding to early irreversible termination of the propagating chain when performing similar chain extensions using poly(MMA-*ran*-S), poly(EMA-*ran*-S) and poly(BMA-*ran*-S), macroinitiators to chain-extend a fresh batch of methacrylate/styrene mixtures.[44] For the synthesized PSMA containing block copolymer; when ignoring the contribution from the terminated macroinitiators, the GPC chromatograms indicate a monomodal shift from PSMA to block copolymer. Therefore, the molecular weight distribution was estimated for the block copolymer, assuming no contribution from the dead macroiniator. The resulting block copolymers were characterized by an increase of the M_w/M_n, from M_w/M_n=1.24 to

1.74-2.06. As mentioned earlier, ^{1}H NMR spectroscopy was used to determine the ratio of methacrylic versus styrene content in the final block copolymer and the obtained values can be found in Table II. In all cases, the final block copolymer contained significantly more respective methacrylate units than styrene ($R_{XMA/S}$=3.30-5.5), which is consistent with the GPC data. The theoretical composition of the XMA/S block was estimated using the reactivity ratios of MMA/S (r_{MMA}=0.58, r_S=0.55),[45] EMA/S (r_{EMA}=0.65, r_S=0.29),[46] BMA/S (r_{MMA}=0.54, r_S=0.64),[46] and BzMA/S (r_{BzMA}=0.51, r_S=0.44).[46] The resulting Mayo-Lewis[47] plots can be found in Figure 3. The styrene composition in the second block was estimated using ^{1}H NMR spectroscopy and plotted for comparison (Figure 3). It is important to note that the molar fraction of styrene in the XMA/S block (F_S) is a little overestimated, which is due to the presence of styrene found in the PSMA block. Compositions given are derived from Mayo-Lewis plots; however, the conversions are relatively high and suggest compositional drift may alter the predicted copolymer composition. However, given that the reactivity ratios are nearly identical between styrene and the methacrylate, a random microstructure is predicted and thus drift would not be significant. These comparisons suggest that the reactivity ratios can be used directly with the Mayo-Lewis equation to estimate the copolymer composition of the second block at low monomer conversion. PSMA macroinitiator was largely successful in synthesizing a narrow molecular weight distribution block copolymer with two distinct blocks: a perfectly alternating reactive segment and a second block consisting of essentially
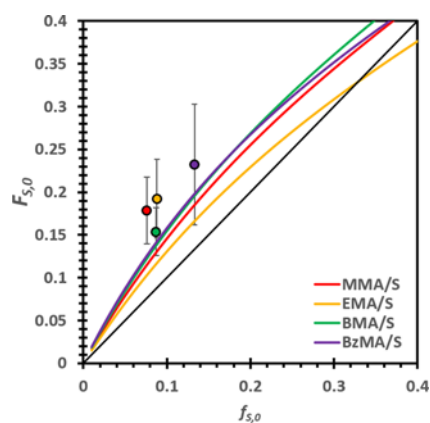

Figure 3. Final styrene composition (F_S) versus initial styrene feed ratio ($f_{S,0}$) in the XMA/S block (XMA/S; X=methyl (M), ethyl (E), *n*-butyl (B) or benzyl (Bz)) chain extensions from poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiator. The solid lines represent the theoretical composition of the XMA block estimated using the Mayo-Lewis[47] equation and the reactivity ratios of MMA/S (r_{MMA}=0.58, r_S=0.55),[45] EMA/S (r_{EMA}=0.65, r_S=0.29),[46] BMA/S (r_{MMA}=0.54, r_S=0.64),[46] and BzMA/S (r_{BzMA}=0.51, r_S=0.44).[46] The filled circles represent the estimated styrene composition in the XMA/S block, given the macroinitiator composition and the yield of the second block. The colours of the filled circles match the solid line, which correspond to the legend in the figure.
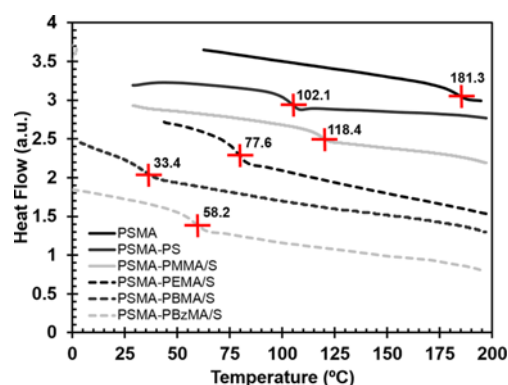

Figure 4. Differential scattering calorimetry (DSC) spectrograms for poly(styrene-*alt*-maleic anhydride) (PSMA) macroinitiator, PSMA-poly(styrene) (PSMA-PS) and PSMA-X-methacrylate/styrene (XMA/S; X=methyl (M), ethyl (E), *n*-butyl (B) or benzyl (Bz)) block copolymer. The spectrograms are from the second heat cycle in a heat/cool/heat experiment. All formulations and characterization data are summarized in Table I and Table II, respectively.

methacrylic species.

Differential Scanning Calorimetry (DSC) Characterization. The glass transition temperatures (T_g) of the PSMA macroinitiator as well as that of all the block copolymers were determined by DSC. Figure 4 shows the DSC traces of the final block copolymers and Table II identifies the corresponding glass transition temperatures (T_g). For PSMA, the measured T_g was 181.3 ºC, corresponding to the literature value for poly(styrene-*co*-maleic anhydride) of similar molecular weight and composition.[28] PSMA-PMMA/S exhibited a T_g= 118.4 ºC, PSMA-PEMA/S exhibited a T_g=77.6 ºC, PSMA-PBMA/S exhibited a T_g=33.4 ºC and PSMA-PBzMA/S exhibited a T_g=58.2 ºC. In all cases, the values obtained are in agreement with literature values for pure corresponding methacrylate homopolymers of similar molecular weight.[48] The reason only one T_g was observed for the block copolymers is most likely due to the difference in length between the PSMA and methacrylate rich blocks. The methacrylate-rich segment is much longer than the PSMA segment and therefore the weak second order transition due to the PSMA block would be much more difficult to detect in the block copolymer. In most cases the T_g was found to be between that of the pure poly(methacrylate) and poly(styrene) (Table II). Regardless, the T_g is dominated by the methacrylic block and shows how readily an essentially methacrylic segment could be combined with a controlled placement of alternating, reactive MA groups in the second segment. This study indicated how readily NMP could be applied to produce block copolymers with highly controlled microstructural features with easily tuned mechanical properties.

Conclusions

A series of relatively low dispersity poly(styrene-*alt*-maleic

anhydride)-*block*-(methacrylate-*ran*-styrene) block copolymers with various methacrylic monomers were successfully synthesized by NMP. The perfectly alternating MA units in the PSMA segment allowed for controlled placement of the MA reactive group, opening the possibility of post- synthesis reactions such as "grafting-to" reactions to permit the synthesis of comb-type block copolymers and other more complex microstructures. The versatility of methacrylate substitution allows the tuning of the mechanical properties of the material as well, thus making this NMP synthesis route a versatile and straightforward way of obtaining highly controlled complex polymeric microstructures.

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