Synthesis and Glass Transition Behavior of High Molecular Weight Styrene/4-Acetoxystyene and Styrene/4-Hydroxystyene Gradient Copolymers Made via Nitroxide-Mediated Controlled Radical Polymerization

Maisha K. Gray,[†] Hongying Zhou,[‡] SonBinh T. Nguyen,[‡] and John M. Torkelson*[,†,§]

Department of Materials Science and Engineering, Department of Chemistry, and Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208

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ABSTRACT: Styrene (S)/4-acetoxystyrene (AS) gradient copolymers were synthesized by moderate-temperature, nitroxide-mediated controlled radical polymerization. Hydrolysis of styrene/4-acetoxystyrene gradient copolymers produced styrene/4-hydroxystyrene (HS) gradient copolymers. Molecular weight (MW) characterization via gel permeation chromatography demonstrated that these materials were made in a "controlled" manner, while intrinsic viscosity measurements revealed that the MWs exceeded 100 000 g/mol, with apparent viscosity-average MW values ranging between 100 000 and 385 000 g/mol, making these materials the first high MW gradient copolymers ever synthesized. Characterization of the glass transition temperature, T_g, revealed different behavior depending on the type of gradient copolymer produced. Using a normal thermal history for measuring T_g by differential scanning calorimetry (DSC), linear gradient copolymers exhibited one T_g, with a value intermediate to the T_gs of polystyrene (PS) and poly(4-acetoxystyrene) (PAS) or poly(4-hydroxystyrene) (PHS). In contrast, "blocky" gradient copolymers with overall S content ≥55 mol % yielded two T_gs, one near the T_g of PS and the other intermediate to the T_gs of PS and PAS or PHS, indicating microphase separation. When the cumulative composition of the "blocky" gradient copolymer was majority AS or HS, only one T_g was resolved, with a value near the T_g of PAS or PHS. For S/AS and S/HS gradient copolymers of identical chain length, overall fractional S content, and strength of gradient, physical aging at 90 °C provided resolution of a second T_g via DSC, allowing comment on how manifestations of microphase separation depend on gradient structure and the strength of the comonomer repulsive interactions.

Introduction

Controlled or "living" free radical polymerization in its several forms, including atom transfer radical polymerization (ATRP),[1−4] reversible addition−fragmentation chain transfer (RAFT),[5] and nitroxide-mediated controlled radical polymerization (NM-CRP),[6−9] has been heavily investigated for the production of polymers with controlled and often novel architecture. Examples include relatively monodisperse homopolymers with functionalized chain ends,[5,10] star polymers,[5,11] hyperbranched or dendritic polymers,[12−14] and polymer brushes.[15] Additionally, many controlled radical polymerization studies[5,16−22] have been devoted to the production of block or random copolymers showing, among other things, that it is possible to produce block copolymers that cannot be synthesized by anionic polymerization (e.g., block copolymers containing 4-acetoxystyrene blocks[22]) and random copolymers with a lower polydispersity than may be achieved by conventional free radical polymerization (ConvFRP).

Controlled radical polymerization also affords the possibility of producing a novel class of materials called gradient copolymers. Gradient copolymers possess a gradual change in repeat unit composition along some fraction (e.g., "blocky" gradient copolymers) or the entire length (e.g., linear gradient copolymers) of the chain and hence have molecular structures intermediate to those of block and random copolymers. Recently, controlled radical polymerization has been identified as the only potentially viable method of addition polymerization to allow for the production of a broad range of gradient copolymers.[23] Synthesis of gradient copolymers has been reported by several research groups.[3−5,20,24−37] In pioneering work, Matyjaszewski and co-workers[20,26−29] synthesized low molecular weight (MW) styrenic and (meth)acrylic gradient copolymers using ATRP. Syntheses of low MW gradient copolymers via RAFT[5] and NM-CRP[25,30] (the latter is also called stable free radical polymerization) have also been demonstrated. Recently, the synthesis of moderately high MW styrene/4-methylstyrene gradient copolymers via NM-CRP and the synthesis of gradient copolymers via ring-opening metathesis polymerization (ROMP) have been described by Gray et al.[37] and Dettmer et al.,[36] respectively.

In addition to the syntheses of gradient copolymers, there has also been theoretical work and speculation regarding the properties and applications of these materials,[38−42] both in the neat and solution states and also as additives to immiscible polymer blends. For example, predictions have been made regarding the impact of gradient architecture on the order−disorder transition and equilibrium microphase-separated morphologies that may be achieved with bulk gradient copolymers.[38,39,41] Additionally, numerical self-consistent-field theory has been employed to describe the equilibrium segregation of gradient copolymers to the interfacial regions of immiscible polymer blends,[40] an issue of importance in the potential application of gradient copolymers in the technologically important field of blend compatibilization.[41−46]

[†] Department of Materials Science and Engineering.

[‡] Department of Chemistry.

[§] Department of Chemical and Biological Engineering.

* To whom correspondence should be addressed: email j-torkelson@northwestern.edu.

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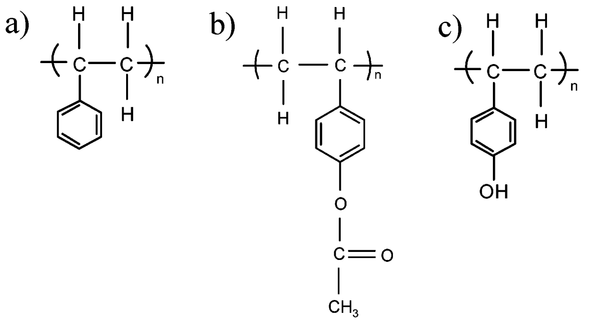

Figure 1. Repeat unit structure of (a) styrene, (b) 4-acetoxystyrene, and (c) 4-hydroxystyrene.

Up to the present time, there has been limited experimental study[20,25,30,32,37,42,47] of the properties of gradient copolymers. These studies have often yielded data indicating similarity of gradient copolymers to either random copolymers or block copolymers. Farcet et al.[25] found that styrene/*n*-butyl acrylate copolymers with MWs < 50 000 g/mol, and weak composition gradients along the chain exhibited a single glass transition temperature, T_g, that decreased with increasing *n*-butyl acrylate content. In contrast, with copolymers exhibiting stronger composition gradients, Matyjaszewski and co-workers[20,28,29,42] demonstrated the presence of microphase separation in low MW styrene/methyl acrylate gradient copolymers (M_n = 12 000 g/mol) using thermal and rheological analysis and in low MW styrene/acrylonitrile gradient copolymers (MWs < 30 000 g/mol) using small-angle X-ray scattering. Buzin et al.[47] have noted that, due to the composition distribution in gradient copolymers, "the repulsive interchain interactions are varying smoothly along the chain", and "these atypical interactions are expected to result in unique thermal properties of the gradient copolymers". However, the systems studied by Buzin et al. were block copolymers with one of the blocks itself a copolymer exhibiting a small gradient in composition, resulting in experimentally measured thermal properties relatively similar to those of block copolymers. Recently, Gray et al.[37] discovered significant differences in the enthalpy recovery behavior of styrene/4-methylstyrene random and gradient copolymers of similar overall composition, providing experimental support for the prediction by Buzin et al.[47]

Here we present a study that combines the synthesis of high MW gradient copolymers (with apparent M_v values of 100 000−385 000 g/mol) by NM-CRP with characterization via differential scanning calorimetry and demonstrates how the behavior of these copolymers is related to the strength of the composition gradient along the chain. We also offer perspectives on the molecular characteristics that may yield gradient copolymers with distinctive properties. Important among these are the strength of the repulsive interactions between comonomer species. In particular, gradient copolymers of styrene/4-acetoxystyrene and styrene/4-hydroxystyrene have been prepared using *N*-(α-methylbenzyloxy)-di-*tert*-butylamine (A−T) as the unimolecular initiator. (See Figure 1 for the repeat unit structures of the monomers.) The A−T initiator was first used by Catala et al.,[48] who found that NM-CRP of styrene could be achieved at moderate temperature with this initiator. Recently, it has been shown[49,50] that the use of A−T at moderate temperature affords the synthesis of high MW polystyrene without loss of control of the polymerization, which can occur readily at high reaction temperature due to thermal self-initiation of monomer. The achievement of high MW may be important in synthesizing gradient copolymers with properties that are not near mimics of random or block copolymers.[41]

Experimental Section

Materials and Methods. Styrene (Aldrich, 99%) and 4-acetoxystyrene (Aldrich, 96%) were deinhibited using *tert*-butylcatechol inhibitor remover and dried over CaH_2 before use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), benzoyl peroxide (BPO), 1,4-dioxane (99+%), and hydrazine monohydrate (98%) were used as received (Aldrich).[51]

Initiator A−T *N*-(α-methylbenzyloxy)-di-*tert*-butylamine) was produced as follows.[51] A solution of di-*tert*-butyl nitroxide (0.91 g, 6.28 mmol) and di-*tert*-butyl peroxyoxalate (∼1.54 g, ∼6.6 mmol) (*Caution*: Potentially explosive! Do not scrape or grind the crystalline grains of this latter reagent while dissolving it.) in ethylbenzene (40 mL) was stirred at 35 °C under a N_2 atmosphere until the characteristic red color of the nitroxide disappeared (ca. 3 h).[52] The reaction mixture was then concentrated to ca. 2 mL by evaporation under reduced pressure at room temperature, and the residue was chromatographed on silica gel using a 1:10 ethyl acetate−hexane ratio, yielding a >90% pure sample of A−T as a colorless oil. The impurity is a mixture of both isomers of 2,3-diphenylbutane that are side products from the synthesis of A−T and cannot be completely separated from the desired A−T product via conventional chromatography. However, these side products are innocuous hydrocarbons and do not influence the subsequent NM-CRP experiments. ^{1}H NMR ($CDCl_3$): δ 1.04 (s, $C(CH_3)_3$, 9 H), 1.31 (s, $C(CH_3)_3$, 9 H), 1.46 (d, J = 6.8 Hz, $CHCH_3$, 3 H), 4.82 (q, J = 6.8 Hz, $CHCH_3$, 1 H), 7.21−7.33 (m, *aromatic Hs*, 5H).

Apparent number-average MW and weight-average MW, M_n and M_w, were determined relative to polystyrene (PS) standards by gel permeation chromatography on a Waters Breeze instrument equipped with three Waters columns (Styragel HMW2, HMW6E, and HR4) using tetrahydrofuran as the eluent and a Waters 2410 differential refractometer as the detector. Twenty-two PS standards (1320−775 000 g/mol) were used for calibration.

Intrinsic viscosities were measured using a Cannon-Ubbelohde viscometer (size 50) in a 30 °C water bath using THF as the solvent.[53] The kinetic energy and shear correction factors were not applicable. Each polymer solution was continuously diluted in the viscometer. For each dilution, multiple flow times were measured, and the average time was computed. Solution densities were determined on the basis of weight percent of solute and solvent present at each dilution. The intrinsic viscosity, $[\eta]$, was determined as the common intercept of η_{sp}/c vs c and $(\ln \eta_{rel})/c$ vs c, where η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, and c is the polymer concentration expressed in g/dL. The apparent viscosity-average MW, M_v, of copolymers was calculated using Mark−Houwink parameters for the homopolymers found in the literature, $[\eta]$ values obtained from the η_{sp}/c vs c plot, and interpolation between M_v values determined for the two homopolymers, with the interpolation being determined by the copolymer composition.[54−56]

Copolymer compositions were determined by ^{1}H NMR spectroscopy using a 500 MHz Varian Inova instrument. For the styrene/4-acetoxystyrene copolymers, ^{1}H NMR ($CDCl_3$): δ 1.1−2.0 (m, $(CH_2-CH)_n$, 6H), 2.1 (s, CH_3, 3H), 6.2−7.5 (m, *aromatic Hs*, 9H). For the styrene/4-hydroxystyrene copolymers, ^{1}H NMR ($CDCl_3$) was used to verify the disappearance of the CH_3 peak at 2.1 ppm associated with the acetyl group.

The T_g of each as-precipitated material was obtained by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC 822 instrument. Dry N_2 with a flow rate of 45 and 55 mL/min was purged through the DSC cell. Sample masses were 1−10 mg. The styrene/4-acetoxystyrene samples were heated at a rate of 10 °C/min to 170 °C. Unless otherwise noted, the samples were held at 170 °C for 10 min to erase any prior thermal history and were then quenched at a rate of 40 °C/min before being reheated at a rate of 10 °C/min. The T_gs are reported as the onset temperature, $T_{g,onset}$, and the temperature at one-half the change in heat capacity, T_g ($^1/_2\Delta C_p$), for the second heating cycle at a rate of 10 °C/min. A similar procedure was followed for styrene/4-hydroxystyrene samples, except that the samples were heated to 200 °C.

Microphase separation was characterized via enthalpy relaxation techniques first described by ten Brinke et al.[57−59] This was conducted as follows for samples comprised of styrene/4-acetoxystyrene: the samples were heated at a rate of 20 °C/min to 170 °C and held at this temperature for 30 min. Next, the samples were cooled at a rate of 40 °C/min to 90 °C, where they were held for various times. Following physical aging, the samples were cooled at a rate of 40 °C/min to 25 °C before being reheated at a rate of 10 °C/min to 170 °C. A similar procedure was followed for styrene/4-hydroxystyrene samples except that they were heated to 200 °C.

Synthesis of Homopolymers. Poly(4-acetoxystyrene) was synthesized via NM-CRP by combining 4-acetoxystyrene (5.30 g, 0.0327 mol) with A−T (0.0046 g, 1.85×10^{-5} mol), purging the mixture with N_2 for 30 min, and then reacting at 96 °C for 12 h. The resulting polymer solution was cleaned via several cycles of dissolution in tetrahydrofuran (THF) and precipitation in methanol, before being dried at 110 °C under vacuum for several hours.

Synthesis of Random Copolymers. Styrene (S)/4-acetoxystyrene (AS) random copolymers were synthesized by ConvFRP and NM-CRP. To synthesize random copolymers via ConvFRP, S was combined with AS in septum-capped test tubes in various mole fractions (total monomer mix = 0.200 mol). Benzoyl peroxide (0.034 g, 0.140 mmol) was added to each tube, and the mixtures were purged with N_2 for 30 min and then polymerized at 90 °C for 45 min, yielding low conversion (typically 5−15%) as determined gravimetrically. The polymer was washed several times via dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours. Using NM-CRP, S/AS random copolymers were synthesized by combining S with AS in septum-capped test tubes in various mole fractions (total monomer mix = 0.200 mol). [A−T] = 2.05×10^{-4} mol/L was added to each tube. Following a 30 min N_2 purge, samples were polymerized at 90 °C for 45 min, yielding low conversion (typically 0.4%−5%) as determined gravimetrically. Polymer was precipitated as described above.

Synthesis of Linear Gradient Copolymers. Following a 30 min N_2 purge, S/AS linear gradient copolymers (described as lingradA in Results and Discussion) were synthesized in semibatch mode at 90 °C in 10% (v/v) cyclohexane with [A−T] = 1.64×10^{-3} mol/L. Styrene and 4-acetoxystyrene were combined with A−T in a septum-capped test tube in a 4:1 ratio of S (9.09 g, 0.0873 mol) to AS (3.50 g, 0.0216 mol). The semibatch polymerization was performed using a syringe pump to deliver 0.06 mL/min of AS to the test tube over 11 h. During the reaction, 1 mL aliquots were withdrawn at various time intervals, yielding gradient copolymers of various composition and molecular weight. The aliquots were precipitated into excess methanol and dried at 110 °C under vacuum for several hours. To ensure complete removal of solvent and monomer, samples were placed in a vacuum oven at 190 °C for 24 h.[60]

Styrene/4-acetoxystyrene linear gradient copolymers (labeled lingradB in Results and Discussion) were also synthesized at 90 °C in a semibatch mode in 10% (v/v) cyclohexane with [A−T] = 2.05×10^{-4} mol/L. Styrene (9.09 g, 0.0873 mol) was combined with A−T in a septum-capped test tube, and the mixture was purged with N_2 for 30 min. The semibatch polymerization was performed using a syringe pump to deliver 0.12 mL/min of AS to the test tube over 2 h. The resulting polymer solution was washed several times by dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours.

Table 1. Molecular Weight, Composition, and Glass Transition Data for the Conventional Free Radical and Nitroxide-Mediated Controlled Radical Polymerizations of Styrene and 4-Acetoxystyrene Random Copolymers at T = 90 °C

free radical polymerization method	mol % styrene in monomer mix	mol % styrene in copolymer	T_g (°C) (±0.3 °C) onset	T_g (°C) (±0.3 °C) $^1/_2\Delta C_p$
ConvFRP	90	89	110.5	113.8
ConvFRP	70	71	111.9	116.3
ConvFRP	40	33	122.4	126.0
ConvFRP	10	6	123.9	128.0
NM-CRP	85	82	107.1	110.2
NM-CRP	65	64	115.4	118.2
NM-CRP	40	39	117.9	121.8
NM-CRP	25	22	121.0	124.3

Table 2. Molecular Weight, Composition, and Glass Transition Data for the Other S/AS Linear Gradient Copolymers and for the S/AS "Blocky" Gradient Copolymers[a]

sample	apparent M_n[b] (g/mol)	apparent M_v[c] (g/mol)	mol % styrene	T_g (°C) (±0.3 °C) onset	T_g (°C) (±0.3 °C) $^1/_2\Delta C_p$
lingradA[d,86]	84 100		25	119.2	123.6
lingradB	57 700	277 000	60	115.9	119.3
lingradC	81 000	293 000	37	121.8	125.4
lingradD	144 700	384 000	23	123.0	126.6
blockygradA	48 000		76	102.6	105.9
				114.4	117.5
blockygradB	59 200		55	102.6	104.9
				115.7	119.0
blockygradC	63 900		35	117.0	121.1
blockygradD	50 200	192 000	49	119.2	123.0
blockygradE	67 000	175 000	25	119.4	124.6

[a] Note: no data are provided on M_w or polydispersity index due to the fact that the GPC data are providing anomalous results likely due to adsorption of the copolymers on the Styragel columns. For further comment, see ref 87. [b] Determined by GPC. [c] Determined by intrinsic viscosity. [d] Sample collected at the end of polymerization, 11 h.

Other S/AS linear gradient copolymers were synthesized using the same temperature, [A−T], and vol % cyclohexane as described above, but without removal of aliquots during reaction. Styrene (9.09 g, 0.0873 mol) was combined with A−T in a septum-capped test tube. Following a 30 min N_2 purge, the semibatch polymerization was performed using a syringe pump to deliver 0.12 mL/min of AS to the test tube over 6 h (for sample labeled lingradC in Table 2) and 10 h (for sample labeled lingradD in Table 2). Polymer was precipitated as described above.

Synthesis of PS Macroinitiator. Polystyrene was made via NM-CRP by combining S (9.09 g, 0.0873 mol) with A−T (0.0021 g, 8.36×10^{-6} mol), purging the mixture with N_2 for 30 min, and then reacting at 90 °C for 2 h. The resulting polymer solution was washed several times via dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours. GPC: M_n = 25 500 g/mol and M_w/M_n = 1.36.

Synthesis of "Blocky" Gradient Copolymers. The S/AS "blocky" gradient copolymers were synthesized by chain extension or bulk polymerization in tandem with semibatch mode. Via chain extension, PS macroinitiator (2.05×10^{-4} mol/L) and S (5.45 g, 0.0524 mol for blockygradA; 2.73 g, 0.0262 mol for blockygradB; 0.91 g, 0.0087 mol for blockygradC) were combined in a septum-capped test tube, and the mixture was purged with N_2 for 30 min. Semibatch polymerization was performed using a syringe pump to deliver 0.12 mL/min of AS to the test tube over 1 h. The resulting polymer solution was washed several times via dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours.

Other S/AS "blocky" gradient copolymers (described as blockygradD in Results and Discussion) were synthesized at 90 °C via combination of bulk S polymerization and semibatch mode in 10% (v/v) cyclohexane with [A−T] = 1.64×10^{-3} mol/L. Styrene (9.09 g, 0.0873 mol) was combined with A−T in a septum-capped test tube. Following a 30 min N_2 purge, the test tube was immersed in the oil bath. After a 2 h bulk PS polymerization, the semibatch polymerization was started using a syringe pump to deliver 0.12 mL/min of AS to the test tube over 4 h. The resulting polymer solution was precipitated as described above.

Hydrolysis of Gradient Copolymers. Hydrolysis was achieved as described by Chen et al.[61] To remove the acetyl groups from the AS along the copolymer chain, copolymer was added to a flask containing a 9:1 volume ratio of 1,4-dioxane to hydrazine hydrate and stirred in a N_2 atmosphere for 6 h at room temperature. The hydrolyzed product was isolated and washed several times with deionized water and then dried at room temperature under vacuum for 3 days.

Synthesis of Block Copolymers. Two S/AS block copolymers were synthesized via NM-CRP. Using BPO and TEMPO, the styrene block was made via a two-step chain extension. First, S (4.545 g, 0.0436 mol) and a 1.3:1 ratio of TEMPO (0.0382 g, 2.44×10^{-4} mol) to BPO (0.0450 g, 1.86×10^{-4} mol) were combined in a 20 mL septum-capped test tube and polymerized at 125 °C for 24 h following a 30 min N_2 purge. Then the resulting polymer (4.001 g, 1.116×10^{-4} mol) was used as a macroinitiator, combined with S (28.82 g, 0.277 mol), and allowed to react further at 125 °C for 45 min. Polymer was washed several times via dissolution in THF and precipitation in methanol before being dried under vacuum at 110 °C for several hours. GPC: $M_n = 43\,200$ g/mol and $M_w/M_n = 1.46$. This polymer (2.009 g, 4.65×10^{-5} mol) was used as a macroinitiator, combined with AS (9.752 g, 0.0601 mol), and reacted at 125 °C for 20 min.[62] Polymer was precipitated and dried as described above. Analysis of the block copolymer (called blockA) by ^{1}H NMR spectroscopy indicated a structure with 82 mol % S and an overall $M_n = 58\,000$ g/mol.

A second block copolymer was synthesized by chain extension from the same PS macroinitiator used to synthesize the "blocky" gradient samples. This PS (0.04961 g, 2.05×10^{-6} mol) was combined with AS (10.6 g, 0.0654 mol) and reacted at 90 °C for 30 min. Polymer was precipitated and dried as described above. Analysis of the block copolymer (called blockB) by ^{1}H NMR spectroscopy indicated a structure with 40 mol % S and an overall $M_n = 85\,100$ g/mol.

Results and Discussion

Before beginning the synthesis of the S/AS gradient copolymers, a couple of preliminary questions needed to be answered: Can high MW 4-acetoxystyrene homopolymers be made via A−T-mediated controlled radical polymerization? What type of polymerization approach (e.g., batch or semibatch) should be employed to design novel gradient copolymers?

Previous work[49] demonstrated that A−T-mediated polymerizations at moderate temperatures resulted in the production of high MW PS. In addressing the first question, it was found that regardless of the conditions employed (e.g., time, temperature, and concentration of A−T), GPC analysis indicated that PAS homopolymers with M_n much greater than 32 000 g/mol could not be produced. This was surprising because other studies[63,64] have shown that the rate of polymerization of AS is larger than that of S, indicating that high MW PAS homopolymers via NM-CRP should be possible.[63−65] To determine whether anomalous MWs were being obtained via GPC, intrinsic viscosity measurements were used to verify MW results.

Intrinsic viscosity measurements were made on the PAS homopolymer whose synthesis is described in the Experimental Section. From GPC, $M_n = 29\,100$ g/mol was obtained. From intrinsic viscosity measurements, $[\eta] = 0.30$ dL/g. Inserting this value into the Mark−Houwink equation, $[\eta] = KM_v^a$, where $K = 1.75 \times 10^{-4}$ dL/g and $a = 0.64$,[55] yielded $M_v = 113\,000$ g/mol. This result reveals that high MW PAS can be made via NM-CRP using A−T as the initiator. It also indicates that the MW results obtained for AS-containing polymers and copolymers via GPC may be anomalously low, possibly due to polymer adsorption onto the Styragel columns,[66] which could result in delayed elution of the PAS homopolymer (and thereby lower apparent MW and larger apparent polydispersities). As a result, the MW values obtained via GPC for copolymers containing AS will be referred to as apparent M_n and M_w and will be used in order to indicate whether there is chain growth with increasing reaction time during NM-CRP. More quantitatively meaningful values of MW for copolymers containing AS units are obtained from intrinsic viscosity measurements, which nevertheless require an interpolation between values of M_v of PS and PAS that may be calculated from the $[\eta]$ value determined for each copolymer.[54,67]

To address the second question, analysis began with the reactivity ratios for ConvFRP of S/AS random or statistical copolymers which are reportedly close to unity, with $r_S = 0.887$ and $r_{AS} = 1.128$.[55] Using these reactivity ratios with the copolymer equation[68] leads to the prediction that, except at very high conversion, batch copolymerization via ConvFRP is nearly azeotropic. That is, the copolymer composition will be nearly identical to the monomer mix composition.

In early studies of low-conversion synthesis of random copolymers by NM-CRP, Hawker and co-workers[69] indicated that such copolymers have a sequence distribution essentially the same as copolymers made by ConvFRP. This suggests that application of the copolymer equation with classical reactivity ratios is valid for copolymerization by NM-CRP. Thus, it would be expected that S/AS gradient copolymers could be produced only by semibatch polymerization where one or both monomers are added continuously or discretely to the reaction mixture, leading to a conversion-dependent monomer mix composition and thereby a chain-length-dependent composition gradient in the copolymers. However, Matyjaszewski[70,71] has recently explained that in controlled radical copolymerization with intermittent activation the relative rates of comonomer consumption may differ from those in ConvFRP, meaning that the expectation stated above may not necessarily be correct.

Hence, it was necessary to determine whether S/AS random copolymers made at low conversion by NM-CRP yield compositions similar to those made by ConvFRP. Results given in Figure 2 and Table 1 indicate that there is good correspondence in the compositions of the copolymers made by these two synthetic routes. Furthermore, the copolymer compositions are in good agreement with those predicted from the copolymer equation using the reactivity ratios from the literature. Thus, it may be concluded that S/AS copolymers possessing a substantial composition gradient can be made only by using the semibatch reaction method, which was subsequently utilized to produce all the gradient copolymers in this study.

The remainder of Results and Discussion is divided into two sections. Section A concerns the synthesis, molecular characterization, and thermal property analysis of linear gradient copolymers. Section B concerns the synthesis, molecular characterization, and thermal property analysis of "blocky" gradient copolymers.

A. Linear Gradient Copolymers. A.1. Copolymer Synthesis and Molecular Characterization. Figure 3 shows apparent M_n values as a function of polymer-

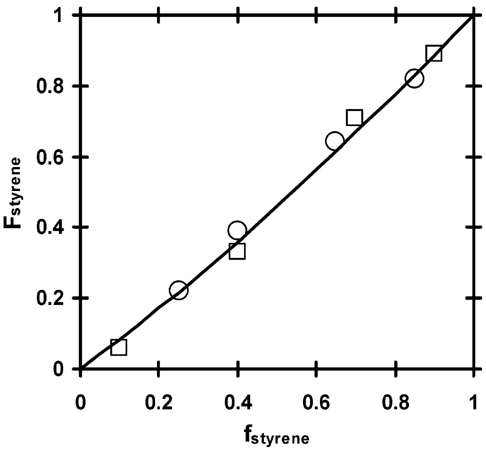

Figure 2. Cumulative copolymer composition, F_{styrene}, as a function of monomer mix composition, f_{styrene}, for S/AS random copolymers made at low conversion via ConvFRP (□) and NM-CRP (○). Also shown are predictions from the copolymer equation (—) using reactivity ratios for styrene (0.887) and 4-acetoxystyrene (1.218) from ref 55.

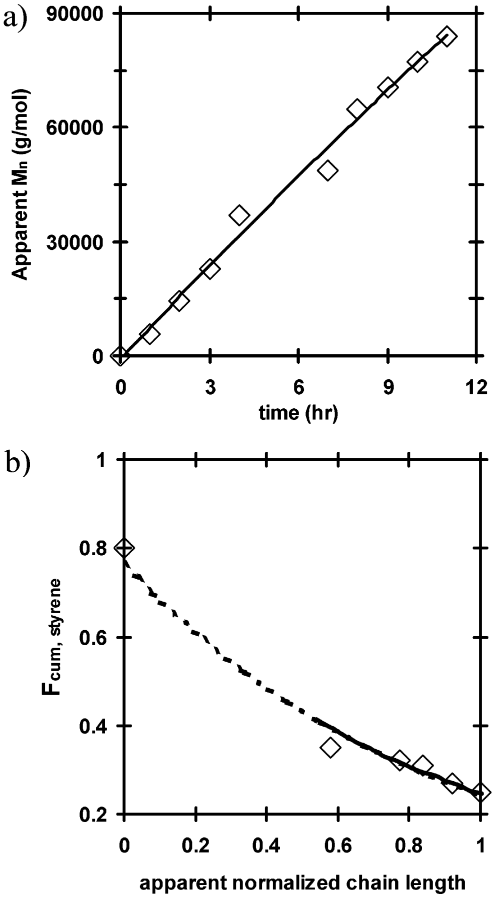

Figure 3. (a) Apparent number-average molecular weight, M_n (○), as a function of polymerization time, t, for sample lingradA. Trendlines are included for M_n (—), showing that M_n increases dramatically and continuously as a function of time. (b) Cumulative styrene composition, $F_{\text{cum,styrene}}$, as a function of apparent normalized chain length for sample lingradA. (Note: normalized chain length is referred to as apparent because it is based on MW results obtained via GPC which may be anomalously low due to adsorption to the GPC column and thus referred to as apparent M_n.)

ization time and the overall styrene mole fraction in a S/AS copolymer, lingradA, made via semibatch mode as a function of normalized chain length. Because of the combination of the small aliquot volumes used for sampling during reaction and the low conversion at low reaction times, insufficient copolymer was recovered at low reaction times to measure copolymer thermal properties or composition. Nevertheless, there is a steady increase in chain length with polymerization time and a significant reduction in overall fractional styrene content in the gradient copolymers as a function of chain length. The former is proof of the synthesis of “controlled” polymer; the latter is proof that the products are gradient copolymers.

As noted for the PAS homopolymer made by NM-CRP, quantitatively meaningful MW data could not be obtained via GPC, although the trend indicating an increase in M_n with time may be taken as proof of the controlled nature of the polymerization over the reaction time of interest. For a more quantitatively meaningful estimate of MW, intrinsic viscosity data were used. For example, for the aliquot removed after a 9 h polymerization for sample lingradA, the apparent M_n and M_w values obtained via GPC were 70 600 g/mol and 103 700 g/mol, respectively, whereas the value of M_v determined from dilute solution viscometry (and interpolation between values of M_v obtained assuming that the polymer was either pure PS or pure PAS)[54−56] is 131 000 g/mol. (The fact that the apparent M_w is less than that of the M_v value can be explained by adsorption of the AS units in the copolymer onto the GPC column.)

Additional proof of the “(pseudo)living” nature of the copolymers is provided by high-temperature annealing of bulk gradient copolymers where interpolymer radical coupling can occur, leading to an increase in apparent M_n values. In the case of the aliquot removed after 9 h, annealing a bulk sample at 170 °C for 10 min resulted in an increase in apparent M_n from 70 600 to 90 100 g/mol. (While the apparent M_n values are not quantitatively accurate, the growth in apparent M_n is indicative in a growth in average molecular weight.) Significant interpolymer radical coupling has been previously demonstrated during annealing of blends containing polymers made via NM-CRP, leading to the production of block copolymer.[43,71]

During the synthesis of sample lingradA, aliquots were removed throughout the reaction to verify the change in overall fractional S content as a function of chain length. Since Figure 3 confirms that semibatch methods yield S/AS gradient copolymers, it was unnecessary to pull aliquots in subsequent polymerizations. Table 2 shows MW and composition data for other S/AS linear gradient copolymers synthesized via semibatch methods starting from a pure S reaction mixture. These samples (lingradB, lingradC, and lingradD) have high MWs, with estimated M_v values between 277 000 and 384 000 g/mol as determined by intrinsic viscosity,[54−56] indicating that NM-CRP can be used to make much higher MW gradient copolymers than previously reported. The controlled nature of the reactions is evidenced by comparison of lingradC and lingradD: lingradC, polymerized for 6 h, has an estimated M_v of 293 000 g/mol, whereas lingradD, polymerized under identical conditions for 10 h, has an estimated M_v of 384 000 g/mol.[54] The overall fractional S content is also a function of reaction time, with more AS being incorporated along the polymer chain with increasing reaction time (e.g., lingradC has an overall composition that is ~37 mol % S after a 6 h polymerization, whereas lingradD has an overall composition that is ~23 mol %

Table 3. Glass Transition Data for the S/HS Gradient Copolymers (Hydrolyzed S/AS Gradient Copolymers)

sample	mol % styrene	T_g (°C) (±0.3 °C) onset	T_g (°C) (±0.3 °C) $^1/_2\Delta C_p$
lingradBhydro	60	140.5	147.1
lingradChydro	37	166.3	172.3
lingradDhydro	23	169.3	175.6
blockygradChydro	35	169.5	174.6
blockygradDhydro	49	156.0	164.3

S after a 10 h polymerization, indicating that one end of the lingradD chain is nearly pure AS). This as well serves as proof of a gradient in composition along the length of the chain that is dictated by reaction conditions.

A.2. Glass Transition Temperatures and Related Thermal Analysis. The T_g data for the S/AS gradient copolymers are shown in Table 2. All samples exhibit single T_gs. In addition, the S/AS linear gradient copolymers have T_g values similar to the random copolymers of comparable composition (and independent of polymerization method). The T_g values in Table 2 are between the T_gs of PS (100 °C) and PAS (125 °C).[72] However, in all cases except for sample lingradB, the T_g values are much closer to the T_g of PAS. These T_gs are reasonable since the samples have incorporated high fractions of AS. All the S/AS gradient copolymers exhibit a narrow breadth of the glass transition (4 °C) as determined by the difference in T_g values obtained by the one-half ΔC_p and onset methods.

Three S/AS gradient copolymers in Table 2 were hydrolyzed to yield S/4-hydroxystyrene (HS) linear gradient copolymers. The T_g data for the S/HS gradient copolymers are shown in Table 3. All samples (lingradBhydro, lingradChydro, and lingradDhydro) exhibit a single T_g, with values between those of PS and PHS (175 °C).[73] The hydrolyzed analogues have a slightly greater breadth of T_g than the unhydrolyzed S/AS copolymers (8 °C for lingradBhydro and ~6 °C for samples lingradChydro and lingradDhydro).

While the single T_gs of the S/AS and S/HS linear gradient copolymers suggested that these materials were not microphase separated, it is possible that these copolymers may have such a small fraction of nanospherical domains within a copolymer matrix that a second T_g is not resolvable by standard DSC analysis. In an attempt to determine more definitively whether these gradient copolymers were microphase separated or not, the enthalpy relaxation method described by ten Brinke et al.[56] was employed.[74] This technique has been used[56−58,75] to study the phase or microphase separation behavior of blends and block copolymers in samples in which there is a close proximity of the homopolymer T_gs or where one of the T_gs may be very weak. With the enthalpy relaxation technique, S/AS and S/HS gradient copolymers are physically aged at temperatures below the T_g of PS. If the copolymers are microphase separated, two physical aging peaks may appear due to the fact that each domain has its own aging behavior.

Within error, only one enthalpy relaxation peak was observed after physically aging the S/AS and S/HS linear gradient copolymers at 90 °C for 24 h, indicating there is no evidence that these copolymers are microphase separated. (See Experimental Section for the enthalpy relaxation protocol. The aging temperature of 90 °C was chosen in order to be below the T_g of any styrene-rich minority domains that may be present in the gradient copolymers.) This result may be rationalized by the facts that the gradient in composition along these copolymer chains is not particularly strong and that a previous study of a gradient copolymer possessing a weak gradient in composition yielded only a single T_g. In particular, Farcet et al.[25] have reported single T_g values for S/*n*-butyl acrylate copolymers possessing weak composition gradients, with the T_g values falling between those of PS and poly(*n*-butyl acrylate) and decreasing with increasing acrylate content at one end of the gradient copolymer.[76]

B. "Blocky" Gradient Copolymers. B.1. Copolymer Synthesis and Molecular Characterization. S/AS gradient copolymers were also synthesized by chain extension of a PS macroinitiator in tandem with semibatch methods. Table 2 shows MW and composition data for the resulting S/AS "blocky" gradient copolymers. Samples blockygradA, blockygradB, and blockygradC were all produced from the same PS macroinitiator (M_n = 25 500 g/mol, M_w/M_n = 1.36). The apparent M_n values of these copolymers range from 48 000 to 64 000 g/mol. However, as discussed for the S/AS linear gradient copolymers, these values are much lower than the true MWs of these samples.[77]

A S/AS "blocky" gradient copolymer was also synthesized by combining bulk polymerization of S with semibatch methods. The MW and composition data for this sample, blockygradD, are shown in Table 2. This sample has an apparent M_v of 192 000 g/mol and an overall composition of 49 mol % S. These results are similar to those obtained for the "blocky" gradient copolymers produced by chain extension, demonstrating that this route is another viable method for gradient copolymer production.

Since the "blocky" gradient copolymers are "(pseudo)-living" materials, they can also be used as macroinitiators to produce yet longer "blocky" gradient copolymers. BlockygradB was used as the macroinitiator (concentration = 2.05×10^{-4} mol/L) in a reaction mixture with 3 mL of AS. As shown in Table 2, blockygradE has an apparent M_v of 175 000 g/mol, with composition decreasing to 25 mol % S from 55 mol % S for the macroinitiator.[78]

B.2. Glass Transition Temperatures and Related Thermal Analysis. Table 2 shows that some of the "blocky" gradient copolymers exhibit two T_gs while others exhibit one T_g. S/AS "blocky" gradient copolymer samples with a cumulative composition greater than or equal to 55 mol % S (i.e., blockygradA and blockygradB) exhibit two T_gs of narrow breadth (~2−3 °C), with one value near the T_g of PS and the other value intermediate to the T_gs of PS and PAS. The presence of two T_g values is indicative of microphase separation in these "blocky" gradient copolymers.

Figure 4 shows DSC thermograms for selected copolymers and demonstrates that the T_gs of the "blocky" gradient copolymers differ slightly from the T_gs of S/AS block copolymers. For example, blockA, with a S composition of 82 mol % and a S block M_n of 43 200 g/mol, had $T_{g,onset}$s of 101.3 and 125.5 °C and $T_g(^1/_2\Delta C_p)$s of 104.5 and 127.2 °C, and blockB, with a S composition of 40 mol % and a S block M_n of 25 500 g/mol, had $T_{g,onset}$s of 100.8 and 121.8 °C and $T_g(^1/_2\Delta C_p)$s of 103.2 and 126.2 °C. The T_gs of the microphase-separated block copolymers are in accord[79] with expectations based on the T_gs of PS and PAS.

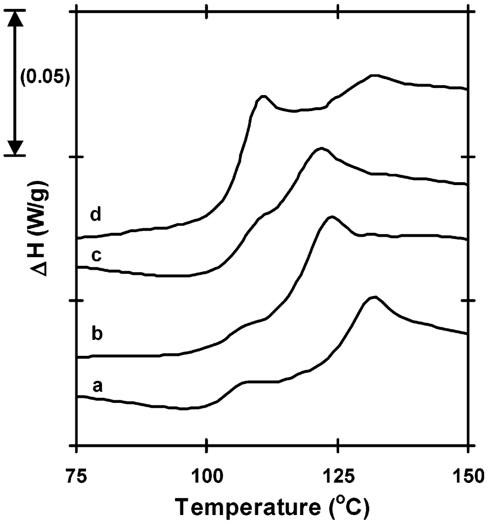

Figure 4. DSC thermograms of S/AS copolymers: (a) block copolymer with 40 mol % S, (b) sample blockygradB, “blocky” gradient copolymer with 55 mol % S, (c) sample blockygradA, “blocky” gradient copolymer with 76 mol % S, and (d) block copolymer with 82 mol % S.

Of the samples in this study, “blocky” gradient copolymers with an overall composition less than 55 mol % S exhibit a single T_g. Samples blockygradC, blockygradD, and blockygradE show only one T_g of narrow breadth (∼4−5 °C), with values close to but below the T_g value of PAS. The T_g data for blockygradE are interesting because this sample was produced via chain extension from blockygradB, a sample that exhibits two T_gs. Thus, one might intuitively expect that blockygradE should have two T_gs as well. However, it is possible that in incorporating substantially more AS along the length of the polymer chain, the AS-rich T_g overwhelms the S-rich T_g, allowing only one T_g to be resolved by conventional thermal analysis.[80]

Two of the S/AS “blocky” gradient copolymers in Table 2 were hydrolyzed, producing S/HS “blocky” gradient copolymers. The T_g data are shown in Table 3. The results are consistent with the T_g data in Table 2 for the unhydrolyzed copolymers; i.e., samples with one T_g still possess one T_g posthydrolysis.[81] The hydrolyzed analogues show T_g results that are similar to those of the unhydrolyzed samples in terms of their proximity to the homopolymer T_gs. However, blockygradDhydro, the hydrolyzed analogue of blockygradD, exhibits a T_g breadth that is double that of the unhydrolyzed S/AS copolymer.

These composition-dependent T_g results suggest that the AS-rich or HS-rich domain T_g (depending on whether the “blocky” gradient copolymer contains S/AS or S/HS) may overwhelm the S-rich domain T_g (if present at all), making it difficult to resolve two T_gs in these gradient copolymer samples.[80] These results further indicate that thermal analysis by conventional DSC methods cannot be solely used to deduce information on the ordered or microphase-separated state of these “blocky” gradient copolymers or other gradient copolymers with a strong composition gradient along the polymer chain. Thus, enthalpy relaxation methods were used with the single-T_g S/AS and S/HS “blocky” gradient copolymers to determine whether it is possible to resolve a microphase-separated state. Following physical aging at 90 °C for 24 h, blockygradD and blockygradDhydro were the only samples where it was possible to resolve the presence of microphase separation based on the presence of two physical aging peaks.[82] Because blockygradD and blockygradDhydro have the same average degree of polymerization, overall S content, and strength of composition gradient, but different repulsive interaction between the comonomers, other aging experiments were performed to determine whether there were differences in the relaxation behavior of these materials. BlockygradD and blockygradDhydro were also aged at 90 °C for 6, 12, and 48 h. Figures 5 and 6 show the DSC thermograms for physically aged blockygradD and blockygradDhydro, respectively. These figures reveal that blockygradD and blockygradDhydro exhibit substantially different enthalpy relaxation behavior, with blockygradD requiring longer physical aging time, 12 h vs 6 h for blockygradDhydro, to reveal the presence of a second aging peak associated with S-rich domains.

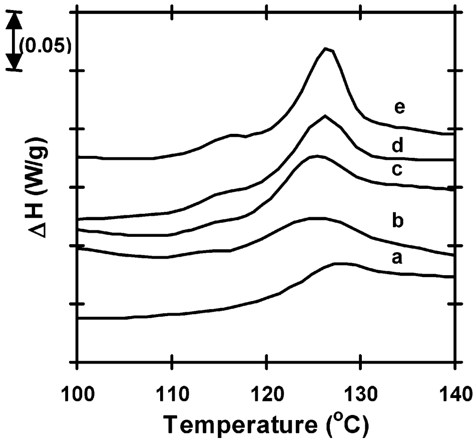

Figure 5. DSC thermograms of blockygradD, a S/AS “blocky” gradient copolymer, after physical aging at 90 °C for (a) 0, (b) 6, (c) 12, (d) 24, and (e) 48 h.

There are two pictures that may be considered for explaining the different time scales at which the physical aging peaks of S-rich domains in microphase-separated S/AS and S/HS blocky gradient copolymers are evident. One is based on the notion that the S-rich domains in the two copolymer systems are nearly pure S in composition, a theoretical possibility due to the presence of S blocks on one end of the copolymers. As a result, one would expect that the aging peaks for the S-rich domains would occur at similar temperatures for the S/AS and S/HS blocky gradient copolymers. However, if there were significantly less of the S-rich domains in one of the copolymer systems, then it would require a longer aging time for the enthalpy relaxation peak to be evident. Comparison of Figures 5 and 6 indicates that the enthalpy relaxation peak of the S-rich domain occurs at lower temperature, indicative of a higher S content in the domain, in the S/HS blocky gradient copolymer system. This result then disallows this simple explanation.

A second picture that may be considered is that there is a substantial difference in the S content of the S-rich domains in the two copolymer systems due significantly to differences in the strength of the repulsive interactions of the comonomer units in the S/AS and S/HS copolymers. This would allow for a difference in the temperatures at which the enthalpy relaxation peaks are evident, consistent with the results of Figures 5 and 6. Then the differences in the time scale at which aging peaks occur may be explained as being a simple manifestation of the inherent difference between the two

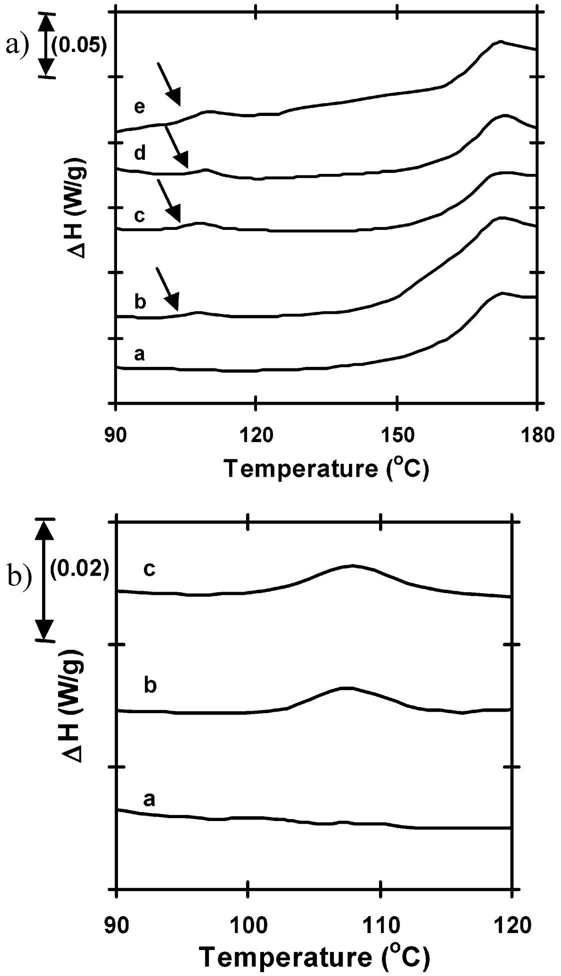

Figure 6. (a) DSC thermograms of blockygradDhydro, a S/HS "blocky" gradient copolymer, after physical aging at 90 °C for (a) 0, (b) 6, (c) 12, (d) 24, and (e) 48 h. Arrows in plot indicate second resolvable peak that results due to physical aging. (b) DSC thermograms of blockygradDhydro with the *x* and *y* axes rescaled to clearly show the second peak that results after aging: (a) 0, (b) 6, and (c) 12 h.

copolymers in the relaxation behavior of the S-rich domains that contain different levels of S and the AS or HS comonomer.

The fact that the relaxation peak of the S-rich domain occurs at lower temperature in the S/HS blocky gradient copolymers, meaning that there is a higher S content in the S-rich domains of the S/HS blocky gradient copolymers, implies that the repulsive comonomer interactions are stronger in the S/HS copolymers than in the S/AS copolymers. To the best of our knowledge, no value for the Flory−Huggins interaction parameter (χ) for the S/HS or S/AS system has been reported in the literature.[83] However, it is logical to expect that the presence of a hydroxyl group on HS will lead to greater incompatibility with S than the presence of an acetoxy group on AS.

Interestingly, the apparently greater repulsive interaction between the comonomers in the S/HS system as compared to the S/AS system has not led to the detection by thermal analysis of the microphase separated in a S/HS gradient copolymers when such a microphase-separated state is absent in a S/AS gradient copolymer of identical chain length, overall composition, and composition gradient. Such an outcome is expected to be possible on the basis of recent theoretical work.[41] Instead, it is likely that the gradient copolymers synthesized in this study were not of the necessary chain length or composition gradient to allow for the difference in comonomer repulsive interactions alone to lead to one system being disordered while the second system is microphase-separated. Further study of such behavior is warranted. Such studies, along with studies comparing micelle formation of gradient copolymers to that of block copolymers[84,85] and determining the utility of gradient copolymers as additives for compatibilizing immiscible polymer blends, are underway.

Conclusions

The synthesis of high MW S/AS and S/HS linear gradient copolymers has been demonstrated. GPC analysis confirmed that the linear gradient copolymers were made in a "controlled" manner, as evidenced by growth in apparent M_n with time. Because of possible adsorption of the AS-containing polymers onto the GPC column, intrinsic viscosity measurements were used to verify that high MW materials were synthesized, with apparent M_v values between 130 000 and 385 000 g/mol. All linear gradient copolymers in this study exhibited single T_gs with values similar to random copolymers of comparable composition and between those of PS and PAS or PHS. Enthalpy relaxation studies reinforced the conclusion that the S/AS and S/HS linear gradient copolymers were not microphase separated.

High MW S/AS and S/HS "blocky" gradient copolymers were also produced, with apparent M_v values between 100 000 and 200 000 g/mol. These materials exhibited two T_gs when the cumulative styrene composition was greater than or equal to 55 mol % S; one T_g was near the T_g of PS, and the second was between the T_gs of PS and PAS or PHS. A single T_g near but below the T_g of PAS or PHS was exhibited when the cumulative styrene composition was less than 55 mol % S. Enthalpy relaxation methods were able to resolve two physical aging peaks, indicative of the presence of microphase separation, in "blocky" gradient copolymer samples with a strong composition gradient that exhibited only one T_g by conventional DSC scanning methods. It was shown that S/AS and S/HS "blocky" gradient copolymers of identical chain length, fractional S content, and composition gradient along the chain exhibit different enthalpy relaxation behavior, with two aging peaks being resolved more quickly in the S/HS "blocky" gradient copolymers.

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(53) These conditions were chosen to mimic conditions of our GPC, which uses THF as the eluent at a temperature of 30 °C.

(54) To obtain M_v for the copolymers, $[\eta]$ taken from the plot of η_{sp}/c vs c was plugged into the Mark−Houwink equation, $[\eta] = KM_v{}^a$, with K and a values for PS and PAS from the literature (see ref 55). These M_v values gave a range for the apparent M_v assuming the polymer was purely PS or purely PAS. These M_v values were converted to number of repeat units and multiplied by the mole fraction of PS and PAS, respectively. Apparent M_v of the copolymer was determined additively based on composition of the copolymer. For example, the $[\eta]$ of sample lingradB was found to be 0.692 dL/g. Assuming the sample was 100% PS, plugging K and a values of 1.27×10^{-4} dL/g and 0.71, respectively, into the Mark−Houwink equation results in a $M_v = 183\,000$ g/mol. Assuming the sample was 100% PAS, plugging K and a values of 1.75×10^{-4} dL/g and 0.64, respectively, into the Mark−Houwink equation results in a $M_v = 417\,000$ g/mol. These two M_v values provide a bound between which the M_v of the copolymer should fall. From these M_v values, the numbers of repeat units are determined to be 1757 and 2573 for PS and PAS homopolymers with $[\eta] = 0.692$ dL/g, respectively. By multiplying the total number of PS repeat units (1757) by the mole fraction of PS in the copolymer (0.60, which can be found in Table 2) and the number of PAS repeat units (2573) by the mole fraction PAS in the copolymer (0.40), an approximation for the number of PS and PAS repeat units in the copolymer is obtained to be 1054 and 1029, respectively. Each of these values is then multiplied by the molecular weight of the PS and PAS repeat units (i.e., 104.15 and 162.19 g/mol, respectively) and added together to produce an apparent M_v value of 277 000 g/mol for sample lingrad.

(55) Brandrup, J. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A., Bloch, D. R., Eds.; Wiley: New York, 1999; p II-263.

(56) It is possible that the values of apparent M_v for copolymers obtained by the interpolation method described in ref 54 may be high limits. The incorporation of S and AS in a single copolymer may lead to THF being an apparently better solvent for the copolymer than for either homopolymer. This is because the incompatibility of the S and AS units may lead the copolymer to be more swollen in THF (i.e., to pervade more volume in dilute solution) than either homopolymer. For related discussion of this issue, see: Rempp, P.; Benoit, H. *Rubber Chem. Technol.* **1968**, *41*, 245−253.

(57) Salomons, W.; ten Brinke, G.; Karasz, F. E. *Polym. Commun.* **1991**, *32*, 185−188.

(58) Oudhuis, A. A. C. M.; ten Brinke, G.; Karasz, F. E. *Polymer* **1993**, *34*, 1991−1994.

(59) ten Brinke, G.; Oudhuis, L.; Ellis, T. S. *Thermochim. Acta* **1994**, *238*, 75−98.

(60) It is important that the solvent and monomer are completely removed from the samples. It has been shown that small percentages of residual solvent and monomer can greatly affect the thermal properties of samples. See: Braun, G.;

Kovacs, A. J. *Compt. Rend.* **1965**, *260*, 2217−2220. Chow, T. S. *Macromolecules* **1980**, *13*, 362−364.

(61) Chen, X.; Jankova, K.; Kops, J.; Batsberg, W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 627−633.

(62) It should be noted that block copolymers synthesized via NM-CRP are normally made via a two-step polymerization. However, the block copolymer sample analyzed here was originally synthesized for other purposes in which a longer PS block was needed than was available. For this reason, a chain extension was performed to extend the PS block before another chain extension was performed to add the PAS block.

(63) Cho, A.; Broadbelt, L. J., unpublished results.

(64) Gopalan, P.; Ober, C. K. *Macromolecules* **2001**, *34*, 5120−5124.

(65) Employing similar temperature and time conditions as used in this study, Gao et al. have demonstrated the synthesis of PAS homopolymers using ATRP, producing polymers with a $M_n = 4800$ g/mol and a $M_w/M_n = 1.11$ as determined via GPC with a Nucleosil column set. Since these PAS homopolymers were synthesized for the eventual use as macroinitiators of block copolymers, it is unclear from the text if low MW polymers were actually desired by the authors. See: Gao, B.; Chen, X.; Ivan, B.; Kops, J.; Batsberg, W. *Polym. Bull. (Berlin)* **1997**, *39*, 559−565.

(66) Adsorption of polymer onto Styragel columns has been seen for other homopolymers and copolymers. See: Wesslen, B.; Wesslen, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 355−362.

(67) The copolymer equation or Mayo−Lewis equation is written as follows: $F_1 = [r_1f_1^2 + f_1f_2]/[r_1f_1^2 + 2f_1f_2 + r_2f_2^2]$, where F_1 represents the composition of monomer 1 added instantaneously to the copolymer, f_1 and $f_2 = 1 - f_1$ represent the mole fractions of monomers 1 and 2, respectively, in the monomer reaction mixture, and r_1 and r_2 represent the reactivity ratios of monomers 1 and 2, respectively.

(68) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686−2688.

(69) Matyjaszewski, K. *Macromolecules* **2002**, *35*, 6773−6781.

(70) Farcet et al. have also recently commented that random copolymers made by controlled radical polymerization should be different than those made by ConvFRP since in controlled radical polymerization, the composition distribution is the same for each chain, whereas in ConvFRP the system may have a composition distribution among the chains. See ref 25.

(71) The coupling reaction of two polymeric radicals in the neat polymer system (see ref 43) must compete effectively with another well-documented reaction of polymeric radicals in the presence of oxygen, that being the production of a terminal ketone. For documentation of the latter reaction, see: Malz, H.; Komber, H.; Voigt, D.; Pionteck, J. *Macromol. Chem. Phys.* **1998**, *199*, 583−588. Dourges, M. A.; Charleaux, B.; Vairon, J.-P.; Blais, J.-C.; Bolbach, G.; Tabet, J.-C. *Macromolecules* **1999**, *32*, 2495−2502.

(72) T_g values for PAS have been reported ranging between 125 and 128 °C with some indication that the T_g does have a dependence on MW. See: Himuro, S.; Sakamoto, N.; Arichi, S. *Polym. J.* **1992**, *24*, 1371−1376.

(73) T_g values for PHS have been reported in the literature ranging between 175 and 190 °C with some indication that the T_g of PHS is MW dependent. See: Zhao, J. Q.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1997**, *30*, 7119−7126. Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1981**, *22*, 473−476. Himuro, S.; Sakamoto, N.; Arichi, S. *Polym. J.* **1992**, *24*, 1371−1376.

(74) Small-angle X-ray scattering was attempted using a Bruker X-ray Instrument to determine whether the materials existed in a microphase-separated state. However, because of the high MW of these samples, the scattering peak possibly associated with structure of the copolymers was unable to be deconvuluted from the scattering peak associated with the beam stop.

(75) Tsitsilianis, C.; Staikos, G. *Macromolecules* **1992**, *25*, 910−916.

(76) Reference 25 states that T_g values were determined at a heating rate of 20 °C/min but does not otherwise provide details regarding the thermal history protocol used for determining T_g values of their gradient copolymers.

(77) The block copolymer samples, whose synthesis is described in the Experimental Section, offer further proof of the inaccurate MW data obtained via GPC for samples that have incorporated substantial AS along the polymer chain length. For the block copolymer with only 18 mol % AS (sample blockA), there is a small difference in the M_n obtained via GPC (52 200 g/mol) and that calculated from ^{1}H NMR (58 000 g/mol). However, for the block copolymer with 60 mol % AS (sample blockB), there is a large difference between the M_n obtained via GPC (49 100 g/mol) and the M_n calculated from ^{1}H NMR (85 100 g/mol).

(78) There was insufficient material to perform intrinsic viscosity measurements for samples blockygradA thru blockygradC. However, since blockygradC and blockygradE have very similar apparent M_n values and cumulative compositions, it can be estimated that they have similar apparent M_v values. This assumption would yield a M_v value >150 000 g/mol for blockygradC.

(79) It should be noted that the small difference in the T_gs of PS and PAS leads to difficulty in accurately ascertaining the $T_{g,onset}$ of the AS-rich microphase in the S/AS block copolymer. As such, the higher $T_{g,onset}$ as reported may be slightly higher than the true value.

(80) DSC samples were prepared to determine whether the PAS T_g overwhelms the PS T_g. For hand-mixed blends of 25/75 wt % PS/PAS, the PAS T_g obtained is more resolvable than the PS T_g.

(81) Sufficient material did not exist to hydrolyze the samples that showed two T_gs due to the low yield of the hydrolysis procedure employed. However, it was assumed that the samples that originally showed two T_gs as S/AS “blocky” gradient copolymers would show two T_gs as S/HS “blocky” gradient copolymers.

(82) The aging times (up to 48 h) used in this study are relatively short in comparison to those used by ten Brinke and others (e.g., 320−666 h). See refs 57 and 75. Therefore, it is possible that a longer aging time may have resulted in the observation of a microphase-separated state for other S/AS and S/HS gradient copolymers in Tables 2 and 3.

(83) As noted by a reviewer, it may be possible to determine the difference in the Flory−Huggins interaction parameter between S/AS and S/HS by making 50/50 random copolymers of S/AS and S/HS and then determining the MW of PS homopolymer that is just miscible with each of the two copolymers. With an appropriate estimate of the copolymer MWs, it would then be possible to estimate the difference in the Flory−Huggins interaction parameters. While 50/50 random copolymers were not made in the present study, future work will be undertaken to address this issue.

(84) Major, M. D.; Brearley, A. M.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 1711−1717.

(85) Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *J. Chem. Phys.* **1989**, *90*, 5806−5825.

(86) Copolymers from the lingradA polymerization collected in aliquots with polymerization times ranging from 7 to 10 h also yielded T_g values that were within 1 °C of those for the sample collected at 11 h.

(87) The polydispersity indexes (PDIs) for the copolymers are not meaningful due to adsorption of the copolymer onto the Styragel GPC columns. Therefore, the PDIs should not be taken to be meaningful in determination of the “livingness” of these materials. Rather, the growth in M_n as a function of polymerization time as well as the observation of interpolymer radical coupling of copolymer chains have been provided as proof the “livingness” of these materials (and the polymerization). However, for the polymerization described by Figure 3, the apparent PDIs ranged from 1.28 to 1.36 for the aliquots removed during the first 4 h and between 1.45 and 1.54 for the aliquots removed during the last 5 h. For the remaining gradient copolymers described in Table 2, the apparent PDIs ranged between 1.68 and 1.94.

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