Uniquely Broad Glass Transition Temperatures of Gradient Copolymers Relative to Random and Block Copolymers Containing Repulsive Comonomers

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ABSTRACT: Nitroxide-mediated controlled radical polymerization is used to synthesize gradient and block copolymers of styrene (S) and 4-acetoxystyrene (AS), and conventional free radical polymerization is used to synthesize S/AS random copolymers. The S/AS copolymers are hydrolyzed to yield S/4-hydroxystyrene (HS) copolymers. Gel permeation chromatography and ^{1}H NMR of aliquots taken during polymerization yield proof of the controlled nature of the gradient copolymer structures. The glass transition temperature (T_g) responses are compared using the derivative of differential scanning calorimetry heat curves, with the temperature range over which the derivative exceeds a base level being equated to the T_g breadth. A single, narrow T_g is obtained in each random copolymer, consistent with a single phase of limited compositional nanoheterogeneity. Two narrow T_gs are evident in each block copolymer, consistent with well-developed nanophases containing nearly pure S or nearly pure AS or HS units with a very narrow interphase yielding no indication of an intermediate T_g. In contrast, T_g breadths of ~65−80 °C are observed in many S/HS gradient copolymers, consistent with ordered nanostructures in which the unit cell composition varies sinusoidally. The possibility of capitalizing on the broad T_g of gradient copolymers in damping applications is discussed.

Introduction

Since the advent of controlled radical polymerization (CRP),[1−3] many novel polymeric materials[4−6] have been synthesized by CRP and studied for scientific interest and technological application. Among the materials made possible by CRP include gradient copolymers, a novel class of materials possessing a gradient in composition from predominantly one monomer species to a second monomer species along the copolymer backbone. Thus, gradient copolymers occupy a material space in which random copolymers and block copolymers form extreme cases, with random copolymers possessing no gradient in average composition along the chain and block copolymers possessing a constant composition along the chain at all but one position (if it is a diblock copolymer) where there is a step change in composition. Gradient copolymers have been synthesized by batch or semibatch (fed batch) reactions involving all major forms of CRP,[7−22] including atom transfer radical polymerization (ATRP), reversible addition−fragmentation transfer (RAFT), and nitroxide-mediated CRP. Gradient copolymers have also been made using ring-opening metathesis polymerization[23] and living cationic polymerization.[24] The applications for which gradient copolymers are well suited range from additives in cosmetics[25] to compatibilizers of immiscible polymer blends.[11,13]

The smooth change in composition along an A−B gradient copolymer chain means that the normally repulsive interchain interactions change smoothly along the chain length, which in turn led Buzin et al.[26] in 2002 to state that gradient copolymers "are expected to result in unique thermal properties." In 2004, Lefebvre et al.[27] used self-consistent mean-field calculations to predict that for symmetric gradient copolymers of sufficiently high χN, where χ is the Flory−Huggins interaction parameter and N is the average number of monomers per chain, ordered lamellar structures will be obtained with a unit cell composition that is sinusoidal and limited in amplitude. In other words, the composition within a lamella is smoothly varying and never reaches pure A or pure B. This is different from A−B random copolymers, which form a single phase without microphase or nanophase separation, and A−B block copolymers, which typically yield ordered structures (also called microphase- or nanophase-separated systems) with domains that are nearly pure A or B with a very narrow interfacial width comparable to several statistical segment lengths.[27] These differences between gradient and other copolymers led Lefebvre et al.[27] to state that the "glass transition... is expected to be very broad for a gradient copolymer... in the case where the A and B homopolymers have very different glass transition temperatures." While a number of studies have noted the presence of one or two glass transition temperatures (T_gs) in various gradient copolymer systems,[7−10,13,15,23,26] none has as yet demonstrated the presence of a uniquely broad T_g in gradient copolymer systems consisting of comonomer units with significant repulsive interactions and in which the homopolymers have very different T_gs.

Here we demonstrate by synthesis and thermal analysis that, in comparison with styrene (S)−4-hydroxystyrene (HS) random and block copolymers, very broad T_g responses are obtainable in S/HS gradient copolymers. The T_g breadths are as large as ~65−80 °C in S/HS gradient copolymers, nearly as large as the ~85 °C difference in T_g values between polystyrene (PS)

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and poly(4-hydroxystyrene) (PHS). Gradient and block copolymers were synthesized by nitroxide-mediated CRP of S with 4-acetoxystyrene (AS), followed by hydrolysis to transform AS to HS. The breadth of T_g was determined with an approach employed beginning in the 1990s by Hourston and coworkers[28−30] and more recently used by Blum[31,32] and Lodge,[33] among others.[34−38] With this method, the T_g breadth can be evaluated from the derivative of the heat curve obtained from temperature-modulated differential scanning calorimetery[28−32,34,37,38] (DSC) or conventional DSC.[33,35,36,38] The temperature range over which the derivative exceeds a base level is equated to the breadth of the T_g response.[28] Along with the scientific significance of the thermal properties of gradient copolymers, we also discuss the technological implications of the broad T_g behavior observed in gradient copolymers.

Experimental Section

Materials and Methods. Styrene (S, Aldrich, 99%) and 4-acetoxystyrene (AS, Aldrich, 96%) were deinhibited using *tert*-butylcatechol inhibitor remover and dried over CaH_2 before use. The unimolecular initiators A−T[9,10,12,39] (*N*-(α-methylbenzoyloxy)-di-*tert*-butylamine) and alkoxyamine 29[6,11] (2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane) were synthesized previously and are the same materials as those used in refs 11 and 12. Polystyrene (Pressure Chemical; nominal MW = 152 000 g/mol, $M_w/M_n = 1.05$) was used as received.

The values of apparent M_n and polydispersity (PDI) for the synthesized (co)polymers were characterized by gel permeation chromatography (GPC, Waters Breeze) relative to PS standards using tetrahydrofuran (THF) as the eluent. Copolymer composition was measured using ^{1}H NMR spectroscopy (Varian Inova 500 MHz) using $CDCl_3$ as solvent. The peak intensities from the NMR spectra associated with the aromatic hydrogens (m, 9H, 6.2−7.3 ppm) and with all other hydrogens (m, 9H, 1.2−2.4 ppm) were compared to NMR spectra obtained from PS and poly(4-acetoxystyrene) (PAS) to determine the S/AS copolymer composition.

Synthesis of S/AS Random Copolymers. Random copolymers of S/AS with different cumulative styrene mole fraction (F_S) were made by conventional batch free radical copolymerization. For example, an S/AS copolymer with $F_S = 0.88$ was prepared using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. A mixture of S (15 mL, 0.131 mol) and AS (2.3 mL, 0.015 mol) was combined with AIBN (0.04 g) in a test tube. Following a 30 min N_2 purge, polymerization was done at 80 °C for 15 min to maintain a low conversion (5% by gravimetry), which prevented drift in the monomer mix composition. The copolymer was washed by several cycles of dissolution in THF and precipitation into methanol and dried under vacuum. See the Supporting Information for preparation of other random copolymers.

Synthesis of S/AS Block Copolymer. Sequential batches of nitroxide-mediated controlled radical polymerization were performed. First, a PS macroinitiator was synthesized using S (20 mL, 0.175 mol) and A−T (1.86×10^{-3} mol/L) at 90 °C for 240 min. This PS macroinitiator (0.4244 g, $M_n = 35\,200$ g/mol, $M_w/M_n = 1.30$) was chain extended with AS (10 mL, 0.065 mol) at 90 °C for 105 min. The resulting polymer was isolated and washed as described above.

Synthesis of S/AS Gradient Copolymers. Semibatch CRP processes using alkoxyamine 29 as the unimolecular initiator were employed in the preparation of gradient copolymers. For the synthesis of a S/AS gradient copolymer with a $F_S = 0.56$ (SgradAS56), styrene (10 mL, 0.087 mol) and alkoxyamine 29 (5.2×10^{-3} mol/L) were combined in a test tube and purged with N_2 for 30 min. To this test tube, AS monomer was delivered at a constant flow rate (3.0 mL/h) during the entire CRP process at 115 °C. To verify the formation of a composition gradient, aliquots (∼1 mL) of the reaction mixture were collected at 1.5, 3.0, and 4.0 h of polymerization time. The copolymers in the aliquot samples were isolated by precipitation into methanol followed by filtration. Each filtered copolymer obtained at different stages of polymerization was dissolved in THF and precipitated into methanol again and dried under vacuum before characterization via GPC and ^{1}H NMR. Finally, the copolymerization was stopped at 5.0 h, and the resulting copolymer (SgradAS56) was isolated and washed as described above. See the Supporting Information for the procedures and characterization results for S/AS gradient copolymers synthesized in this study.

Hydrolysis of PAS and S/AS Copolymers. The S/AS copolymers and PAS homopolymer were hydrolyzed to obtain S/4-hydroxystyrene (HS) copolymers and poly(4-hydroxystyrene) (PHS) using a method described previously.[9,40] The S/AS copolymers and PAS were dissolved in a flask containing a 9:1 v/v 1,4-dioxane/hydrazine hydrate mixture. Each mixture was stirred under N_2 atmosphere for 6−7 h at room temperature. Hydrolyzed product was collected after washing several times with deionized water and placed under vacuum at 50−60 °C for 3 days. Complete hydrolysis of the acetoxy groups was confirmed by NMR analysis, which revealed the loss of the acetoxy hydrogen peak near 2.27 ppm.

Preparation of Blends of S/HS Random Copolymers. Equal weights (each ca. 30 mg) of S/HS copolymers containing 37 and 71 mol % S were dissolved into THF and cast on an aluminum dish. The solvent was allowed to evaporate at room temperature, and the cast blend of random copolymers was further dried under vacuum at 70 °C for a day. A second blend of S/HS random copolymers containing 19 and 88 mol % S was prepared in the same manner.

Thermal Characterization of Copolymers. Thermal analysis was done with a differential scanning calorimeter (DSC, Mettler-Toledo DSC 822e), calibrated with an indium standard, and using sample masses of 2−6 mg. Dry N_2 was passed (50−55 mL/min) through the DSC cell during measurement. The homopolymer and copolymer samples were heated at a rate of 10 °C/min to 180 °C (or to 220 °C for samples containing HS repeat units) and held at temperature for 30 min to erase the thermal history. Each sample was then cooled to 25 °C at a rate of 40 °C/min and reheated to 180 °C (or to 220 °C) at a rate of 10 °C/min (second heat). Data associated with the glass transition were extracted from the second heat scan. All measurements were repeated twice. For each blend of S/HS random copolymers, an additional heating scan (third heat; 10 °C/min) was also employed after isothermal annealing at 220 °C for 180 min prior to quenching to 25 °C (at a cooling rate of 40 °C/min).

Results and Discussion

Synthesis of Gradient Copolymer and Proof of the Composition Gradient. Controlled radical polymerization allows for the synthesis of gradient copolymers owing to its pseudo-living nature and the facile cross-propagation of polymeric free radicals,[7] especially when the synthesis is carried out in a fed batch or semibatch manner.[9−13] In a semibatch CRP involving the addition of a second comonomer to a first comonomer, the cumulative mole fraction of the first comonomer in the resulting gradient copolymer will decrease as the chain length increases.

Figure 1 provides the proof of the gradient structure via the evolution of cumulative styrene mole fraction (F_S, determined from NMR) as a function of apparent normalized chain length for all five S/AS gradient copolymers synthesized and characterized in this study. (The apparent normalized chain length is determined by the ratio of the apparent M_n value of a given aliquot taken at a particular time in the copolymerization to the apparent M_n value of the final gradient copolymer product at the end of the copolymerization.) The composition gradient along each copolymer chain length is consistent with expectations associated with a semibatch copolymerization of S and AS. The final F_S and apparent M_n values of the gradient copolymers range from 0.39 to 0.71 and 75 600 to 127 100 g/mol, respectively.

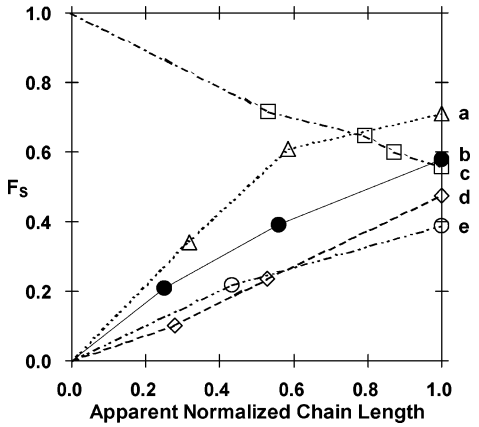

Figure 1. Cumulative styrene mole fraction (F_S) as a function of apparent normalized chain length for SgradAS71 (a, open triangles), SgradAS58 (b, filled circles), SgradAS56 (c, open squares), SgradAS47 (d, open diamonds), and SgradAS39 (e, open circles).

To simplify further discussion, each gradient copolymer will be designated as follows: SgradAS56 (S/AS gradient copolymer with $F_S = 0.56$) or SgradHS56 (S/HS gradient copolymer with $F_s = 0.56$, obtained after hydrolysis of SgradAS56). Random and block copolymers will be similarly designated: SranHS57 (S/HS random copolymer with $F_S = 0.57$, obtained after hydrolysis of SranAS57), SblockAS56 (S/AS block copolymer with $F_S = 0.56$), and so on. See the Supporting Information for detailed results for the synthesis of gradient copolymers.

Comparison of the Breadth of T_g in Gradient, Block, and Random Copolymers and in Homopolymers. Before discussing the T_g behaviors of copolymers, we begin with the T_g analysis of homopolymers. To facilitate the comparison of the breadth of T_g among various polymer systems, we employ the first derivatives of DSC heating curves with respect to temperature. Derivatives of heat curves (or, equivalently, derivatives of heat capacity) have been applied in temperature-modulated DSC (TMDSC)[28−32,34,37,38] and conventional DSC[33,35,36,38] to characterize complex thermal behaviors in polymer blends and block copolymers. (While this approach is one step more complex than simple determinations of T_g widths obtained from DSC heat curves by measuring the temperature range over which there is an apparent change in heat capacity from a glassy state to a rubbery state,[41,42] it provides more precise results when the T_g response is very broad and thus somewhat weak over certain ranges of temperature.[43]) Specifically, the derivatives of heating curves can be effectively utilized for the determination of T_g breadth by defining the onset point of the deviation in the response from the baseline[28] (T_0) and the end point of the T_g peaks. Since our T_g data are collected in a conventional DSC, there are small endothermic peaks from the original DSC heating curves due to enthalpy relaxation (see Figure 2a), which are manifested as downward peaks (or local minima) in the corresponding derivatives (see Figure 2b). (In TMDSC measurements, these small relaxation peaks are usually absent.[28−30,44]) We designate these "negative" peak points (or local minima in the derivative values) as the end point T_g (T_e) for each system. Accordingly, the breadth of T_g is evaluated as the difference between T_e and T_0. The approach for T_g breadth determination is illustrated in Figure 2b. The breadth of T_g (ΔT_g) for each homopolymer is similar, ranging from 14.5 to 18.1 °C, and the T_g values increase in the order from PS to PAS to PHS. See Table 1 for a summary of homopolymer T_g results, which includes a listing of T_{peak} values associated with maxima in the derivatives of heat curves.

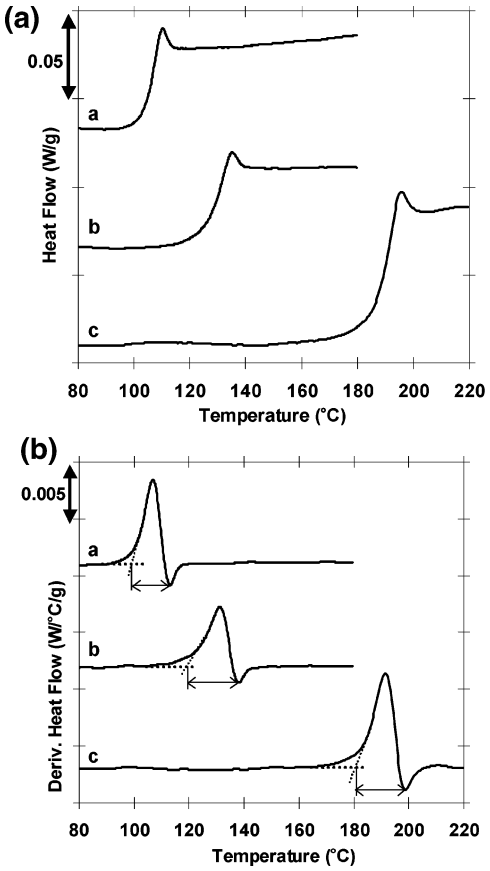

Figure 2. DSC heating curves (a) and the derivatives of DSC heating curves (b) for homopolymers (**a**, PS; **b**, PAS; **c**, PHS). Also shown in (b) is the schematic of the T_g breadth determination.

Figure 3a,b provides the DSC heat curves and the derivative heat curves for S/AS block, random, and gradient copolymers with similar F_S values (0.56−0.58). Similar to the homopolymers, the block and random copolymers exhibit relatively narrow T_g responses. The block copolymer (SblockAS56) exhibits two distinctively discernible T_gs (curve **a** in Figure 3a,b) with ΔT_gs of ∼15 and 21−22 °C, and the random copolymer (SranAS57) shows a single, sharp T_g with a ΔT_g of ∼17 °C (curve **b** in Figure 3a,b). In contrast, the S/AS gradient copolymers (SgradAS56 and SgradAS58; **c** and **d** from parts a and b of Figure 3, respectively) exhibit slightly broader glass transition regions, with ΔT_g being ∼25 °C. The limited additional breadth in the S/AS gradient copolymers as compared with the S/AS block and gradient copolymers is associated with the relatively small difference in the PS and PAS homopolymer T_g values. Table 1 provides a summary for the T_g data associated with Figure 3.

In contrast with the S/AS gradient copolymers, much more substantial differences in T_g breadth are apparent in the S/HS gradient copolymers as compared with the S/HS random and block copolymers. See Figure 4 and Table 1. These substantial differences are made possible by the combined effects of the large differences in PS and PHS homopolymer T_gs as well as the approximately sinusoidal composition profiles predicted by Lefebvre et al.[27] to be found in ordered gradient copolymers. (Recall that the S/HS copolymers are made by direct hydrolysis of the S/AS copolymers, so the comonomer sequences are identical in the S/AS and S/HS copolymer systems except that HS substitutes for AS.)

In particular, Figure 4 and Table 1 show that SblockHS56 (see curve **a** in Figure 4) results in two distinct and vastly

Table 1. Summary of Glass Transition Temperature Data (±0.5 °C) for Figures 2 (Homopolymers), 3 (S/AS Copolymers), and 4−6 (S/HS Copolymers)

sample	F_S	M_n (g/mol)	$T_{g,onset}$[b] (°C)	T_0 (°C)	T_e (°C)	T_{peak}[c] (°C)	ΔT_g (°C)
PS	1	152 000	103.2	98.6	113.1	107.0	14.5
PAS	0	106 700	126.8	120.1	138.1	131.3	18.0
PHS (hydrolyzed PAS)	0		186.6	180.7	198.8	191.5	18.1
SblockAS56	0.56	78 200[a]	103.2	98.1	113.0	106.5	14.9
			122.1	113.0	134.5	126.8	21.5
SranAS57	0.57	47 800	113.8	107.6	124.5	117.8	16.9
SgradAS56	0.56	93 800	107.6	103.9	128.8	112.2	24.9
SgradAS58	0.58	75 600	112.9	107.0	131.8	117.1	24.8
SblockHS56	0.56		101.7	97.5	112.0	106.5	14.5
			187.0	181.6	199.9	192.2	18.3
SranHS57	0.57		140.9	136.4	150.8	144.0	14.4
SgradHS56	0.56		106.6	101.3	171.2	*c*	69.9
SgradHS58	0.58		126.9	121.1	190.3	*c*	69.2
SranHS37	0.37	54 900[a]	162.1	156.0	173.1	166.5	17.1
SgradHS39	0.39	127 100[a]	132.4	124.1	190.8	*c*	66.7
SranHS71	0.71	74 700[a]	122.3	116.9	132.5	125.8	15.6
SgradHS71	0.71	80 100[a]	107.5	105.0	183.2	*c*	78.2

[a] Characterized using S/AS precursors. For SblockAS56, the M_n value was determined by the M_n of PS macroinitiator and the F_S value (0.56). [b] The onset glass transition temperature as evaluated from a conventional DSC heating curve. [c] The peak temperatures from derivatives of DSC heating curves. For S/HS gradient copolymers, multiple peaks are observed.

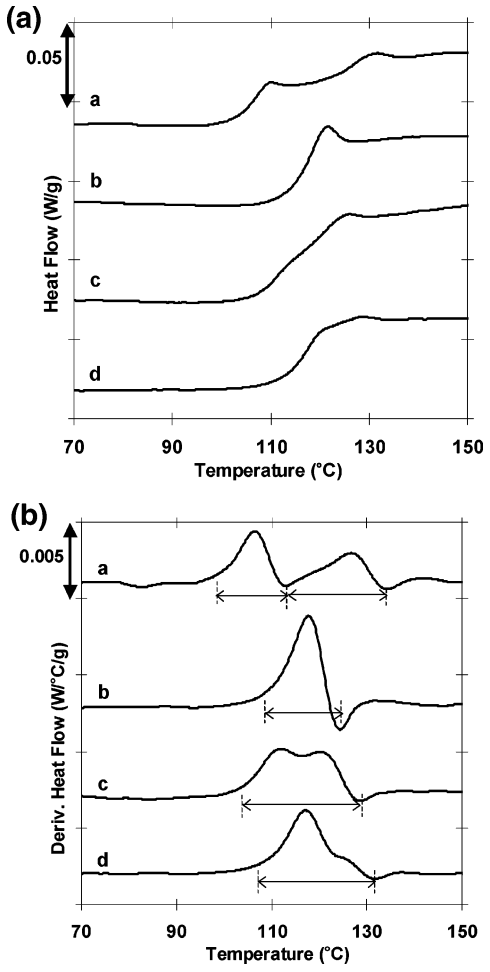

Figure 3. DSC heating curves (a) and the derivatives of DSC heating curves (b) for S/AS copolymers with $F_S = 0.56-0.58$ (**a**, SblockAS56; **b**, SranAS57; **c**, SgradAS56; **d**, SgradAS58). Arrows in (b) indicate the breadth of T_g for respective samples.

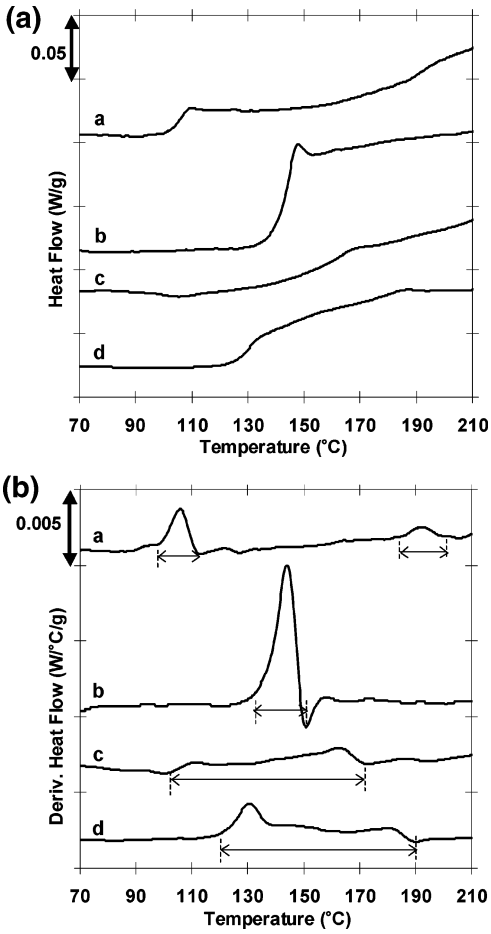

Figure 4. DSC heating curves (a) and the derivatives of DSC heating curves (b) for S/HS copolymers with $F_S = 0.56-0.58$ (**a**, SblockHS56; **b**, SranHS57; **c**, SgradHS56; **d**, SgradHS58). Arrows in (b) indicate the breadth of T_g for respective samples.

different T_gs, with each T_g breadth comparable to that of each homopolymer (PS and PHS). This result is consistent with well-developed microphases containing nearly pure S or nearly pure HS units, with a very narrow interphase region that does not yield any discernible signature of an intermediate T_g. The SranHS57 yields a sharp, single T_g (ΔT_g = 14−15 °C) characteristic of the absence of microphase separation (see curve **b** in Figure 4). In contrast, both SgradHS56 and SgradHS58 exhibit very broad T_g regions ($\Delta T_g = \sim 70$ °C) that cover most of the range between the PS and PHS homopolymer T_gs.

While the T_g breadths are similar in magnitude between SgradHS56 and SgradHS58, there are differences in their T_g behaviors that are consistent with the detailed synthesis ap-

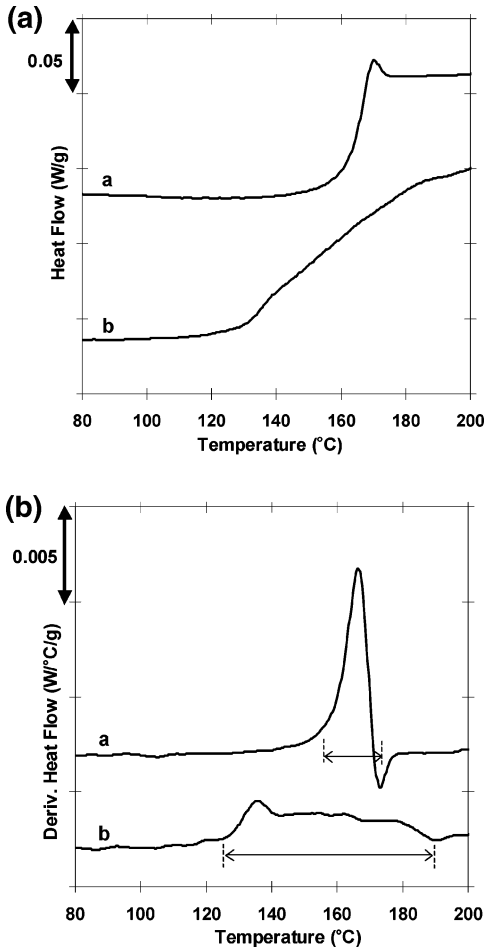

Figure 5. DSC heating curves (a) and the derivatives of DSC heating curves (b) for S/HS random and gradient copolymers with $F_S = 0.37-0.39$ (**a**, SranHS37; **b**, SgradHS39). Arrows in (b) indicate the breadth of T_g for respective samples.

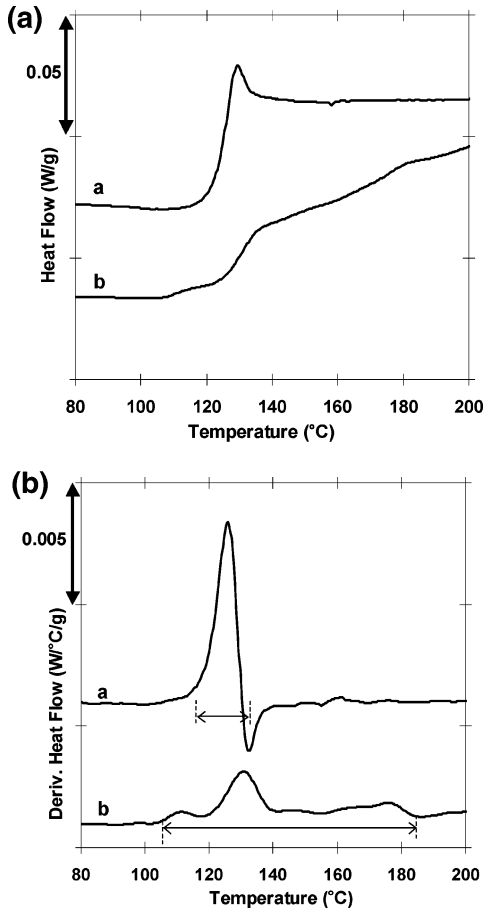

Figure 6. DSC heating curves (a) and the derivatives of DSC heating curves (b) for S/HS random and gradient copolymers with $F_S = 0.71$ (**a**, SranHS71; **b**, SgradHS71). Arrows in (b) indicate the breadth of T_g for respective samples.

proaches used in making these two gradient copolymers. Because SgradHS56 was synthesized in a semibatch reaction in which AS comonomer (later hydrolyzed to HS) was added at a constant rate to styrene, SgradHS56 has one chain end that is very nearly pure S. However, it is likely that the other chain end, while containing much more AS comonomer than S, does not consist of very nearly pure AS comonomer. This is because the S concentration in the monomer mix never reaches zero even at the latest stage of the reaction. Thus, SgradHS56 exhibits a T_0 value close to that of the T_g region of PS with a T_e value significantly lower than the T_g region of PHS. For SgradHS58, the situation is reversed because the copolymer was synthesized in a semibatch reaction in which S was added to AS comonomer (later hydrolyzed to HS). Thus, SgradHS58 exhibits a T_e value close to that of the T_g region of PHS, with the T_0 value being substantially higher than the T_g region of PS. These detailed differences between SgradHS56 and SgradHS58 are not nearly as apparent in the prehydrolyzed, S/AS precursor forms, which is likely due to the proximity of the T_g values for PS and PAS homopolymers.

There is one other noteworthy difference in the derivative heat flow curves of SgradHS56 and SgradHS58. Both curves indicate the presence of two or more local maxima; these may be associated with the relative lengths of runs of nearly common composition that are present within the gradient copolymer chains and the relative size of the change in heat capacity per monomer unit associated with regions of common composition undergoing a glass-to-liquid transition. However, in the case of SgradHS56, the highest value of the derivative heat flow curve is found near the high-temperature end of the T_g breadth while in the case of SgradHS58 the highest value of the derivative heat flow curve is found near the low-temperature end of the T_g breadth. These highest values of the derivative heat flow curves correspond to the final regions of the copolymer chains made during the controlled radical copolymerization. (Recall that the SgradAS56 precursor to SgradHS56 was made by a semibatch method involving addition of AS to S and that the SgradAS58 precursor to SgradHS58 was made by a semibatch method involving addition of S to AS.) Similar observations are evident in the derivative heat flow curves for the other S/HS gradient copolymers discussed below. Further study is warranted to understand the apparent relationship between which comonomer is added during semibatch copolymerization and the location of the highest value of the derivative heat flow curve of the resulting gradient copolymer.

Figures 5 and 6 provide further comparison of the T_g breadths of S/HS gradient copolymers with those of other S/HS random copolymers. Figure 5 shows DSC curves and derivative heat curves for SranHS37 and SgradHS39. The SgradHS39 exhibits a T_g breadth that is nearly a factor of 4 larger than that of the SranHS 37. (See Table 1 for details.) Figure 6 shows DSC curves and derivative heat curves for SranHS71 and SgradHS71, with the gradient copolymer exhibiting a T_g breadth ($\Delta T_g = 78$ °C) that is about a factor of 5 larger than that of the SranHS71 ($\Delta T_g = 16$ °C). In particular, the remarkably large ΔT_g value of 78 °C for SgradHS71 is nearly equal to the difference in the T_g values of PS and PHS. (See Table 1.)

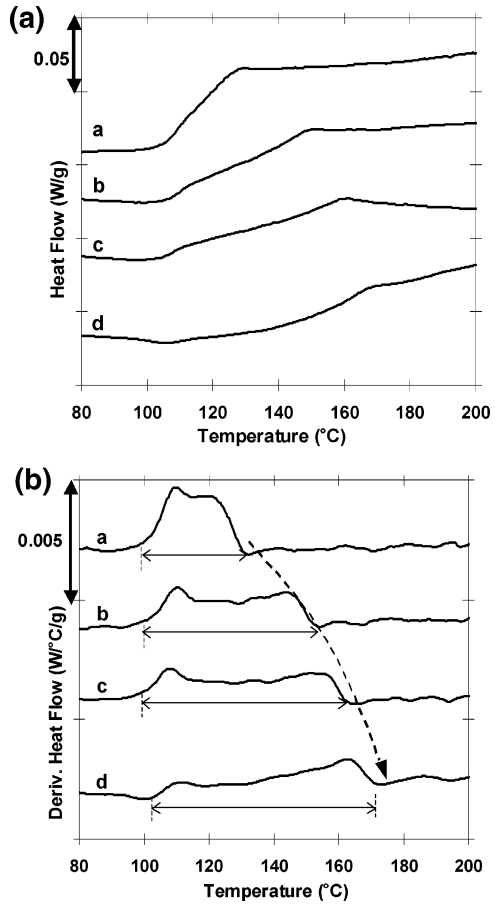

Figure 7. DSC heating curves (a) and the derivatives of DSC heating curves (b) for aliquot samples (taken during gradient copolymerization and then hydrolyzed) and the final SgradHS56 sample. (Note that the final SgradHS56 sample is the same as that in Figure 4, curve **c**.) Arrows in (b) indicate the breadth of T_g for respective samples. The broken arrow in (b) is drawn to indicate the increase in T_e as the gradient copolymerization proceeds. See Table 2 for the characterization and the glass transition data of each sample.

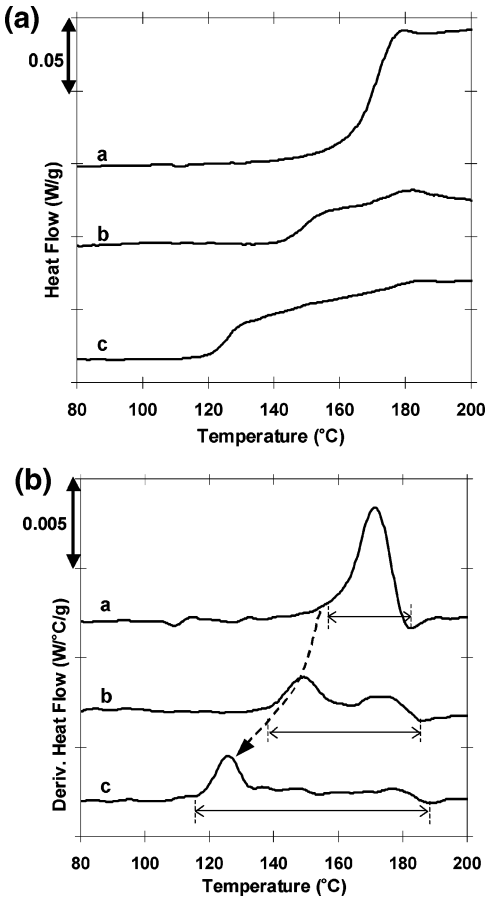

Figure 8. DSC heating curves (a) and the derivatives of DSC heating curves (b) for aliquot samples (taken during gradient copolymerization and then hydrolyzed) and the final SgradHS47 sample. Arrows in (b) indicate the breadth of T_g for respective samples. The broken arrow in (b) is drawn to indicate the reduction in T_0 as the gradient copolymerization proceeds. See Table 2 for the characterization and the glass transition data of each sample.

The Broad T_g in S/HS Gradient Copolymers: Its Origins and Technological Implications. The results in Figures 2−6 show that S/HS gradient copolymers with F_s values ranging from 0.39 to 0.71 exhibit much broader glass transition regions than the corresponding S/HS diblock or random copolymers. These results are consistent with predictions by Lefebvre et al.[27] of sinusoidally varying composition profiles in ordered, lamellar gradient copolymers. Is the picture by Lefebvre et al.[27] the only possible one to allow for such broad, continuous T_gs? No, other types of polymer-based systems have provided indications of a broad distribution of T_g values. These include the trivial, such as physical mixtures of many component blends,[28] and the more complex, such as the reportedly broad glass transition regions associated with nanodomains and interfacial regions containing S units in S−isoprene−S and S−butadiene−S block copolymers.[28,37] Broad distributions of T_g response have also been reported in confined polymer systems with substantial polymer−air or polymer−substrate interfaces,[31,32,45] some miscible polymer blends,[30,38,46] disordered S/*n*-butyl acrylate (*n*BA) block copolymers,[38,46] and ordered S/*n*BA block copolymers involving very weak segregation and broad interfacial width.[38] In particular, in a recent study involving a weakly segregated, ordered S/*n*BA block copolymer, Miwa et al.[38] found two peaks in their derivative heat capacity curves (at −40 to −45 °C and at 80 to 85 °C) but with a breadth to each that provided for a small overlap between the peaks at an intermediate temperature. However, there has not been a previous report of an unusually broad T_g response involving a copolymer system containing comonomer units with strongly repulsive enthalpic interactions, such as those present in S/HS copolymers.[47] (The enthalpic penalty associated interaction of S and HS units has been reported in ref 47 to be extraordinarily high, with a χ value of 6. As the critical point for the order−disorder transition of fully tapered, linear gradient copolymer melts has been predicted[27] to correspond to $\chi N = 29.25$, this means all the S/HS gradient copolymers in this study are fully expected to exhibit ordered rather than disordered structures. The characterization of the ordered structures obtained in S/HS gradient copolymers is beyond the scope of the present study but is planned for the future using small-angle X-ray scattering methods.)

Figures 7 and 8, which show the evolution of the T_g breadth in S/HS gradient copolymers as a function of normalized chain length, provide evidence that the breadth in T_g observed in the S/HS gradient copolymers is a direct consequence of the composition gradient along the chain. In the case of Figure 7, data were obtained by measuring the T_g breadths of SgradHS56 (made by hydrolysis of SgradAS56) as well as of aliquots taken during the semibatch gradient copolymerization of SgradAS56. The copolymer samples from the aliquots, which can be considered to be "partial" gradient copolymers, were isolated and hydrolyzed to yield S/HS copolymers with different overall chain lengths and overall changes in composition. In the early stage (1.5 h) of the gradient copolymerization, the growing

Table 2. Summary of Glass Transition Temperature Data (±0.5 °C) for Figures 7 and 8

DSC curves provided in	CRP stage (h)	F_S	M_n (g/mol)[a]	T_0 (°C)	T_e (°C)	ΔT_g (°C)
Figure 7	1.5	0.72	49 700	100.2	132.2	32.0
	3.0	0.65	74 200	100.4	154.2	53.8
	4.0	0.60	81 700	99.2	164.6	65.4
	5.0	0.56	93 800	101.3	171.2	69.9
Figure 8	1.5	0.10	32 700	156.9	183.8	26.9
	3.0	0.24	61 800	138.4	185.9	47.5
	6.5	0.47	117 200	116.9	187.3	70.4

[a] Characterized using S/AS precursors.

copolymer chains cannot have a full gradient in composition varying from S to HS, and as a result, the T_g response is relatively close to but significantly broader than that of PS. (See curve **a** in Figure 7a,b.) As the compositional gradient builds across the copolymer chain length during the semibatch reaction involving a gradual incorporation of HS (resulting after hydrolysis of AS) into the copolymer, there is a gradual increase in the T_g response at temperatures approaching those of pure PHS without a loss of T_g response at lower temperature associated with the T_g of PS. (See curves **b**−**d** in Figure 7a,b.) As a result of the continuously propagating glass transition across the microphase domains, a T_g breadth of ∼70 °C is exhibited from the final gradient copolymer, SgradHS56. (For the quantitative details on the change in ΔT_g as a function of temporal development of the copolymer structure during the gradient copolymerization, see Table 2.)

Figure 8 shows an equivalent result to that provided in Figure 7 but one in which the direction of T_g breadth development with copolymerization time is reversed from Figure 7. This is because the semibatch gradient copolymerization involves the continuous addition of S to a reaction mixture that initially contained only AS. With the gradual incorporation of S into the copolymer as gradient copolymerization proceeds (from curve **a** to **c** in Figure 8a,b), the T_0 values of the S/HS copolymer samples move toward the PS T_g with the T_e values remaining nearly stationary and close to the T_g region of PHS. (See Table 2.)

Thus, the T_g analyses in Figures 7 and 8 of both gradient copolymer samples taken during different stages of gradient copolymer syntheses are qualitatively consistent with the conclusion of Lefebvre et al.[27] regarding the sinusoidal composition profile of the unit cell in the ordered gradient copolymers. As the copolymer composition varies with growth of the gradient copolymer chain from one stage to another, there is simply an addition of the T_g response associated with the added copolymer composition to the T_g breadth that was initially there.

To further elucidate the uniqueness of T_g broadening in S/HS gradient copolymer systems, we provide a comparison to the T_g behaviors of blends of S/HS random copolymers. For this, we have paired two random copolymers of equal weights,

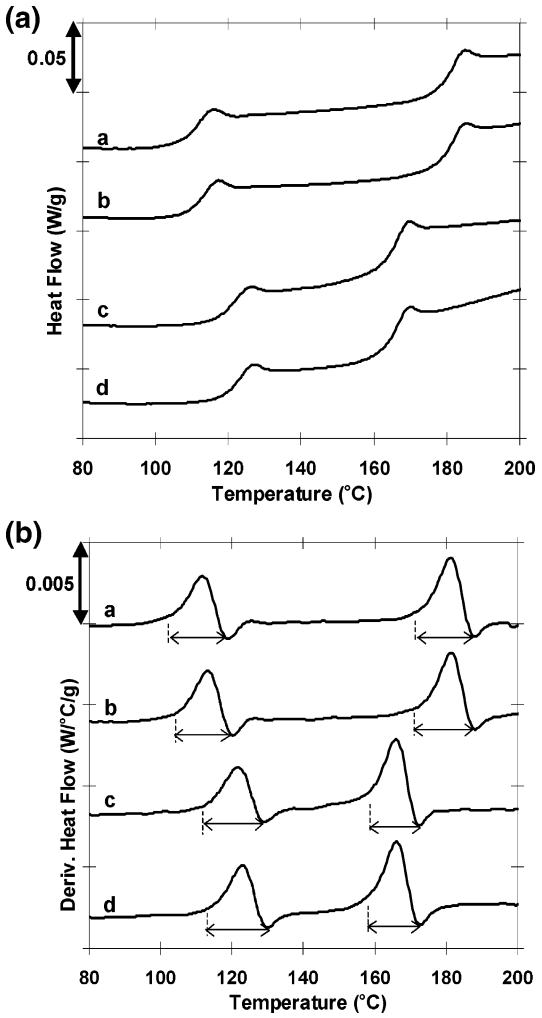

Figure 9. DSC heating curves (a) and the derivatives of DSC heating curves (b) for blends of S/HS random copolymers (**a**, second heat of the SranHS19/SranHS88 blend; **b**, third heat of the SranHS19/SranHS88 blend; **c**, second heat of the SranHS37/SranHS71 blend; **d**, third heat of the SranHS37/SranHS71 blend). Arrows in (b) indicate the breadth of T_g for respective samples. (Note: the third heat scan was performed after annealing each blend sample at 220 °C for 180 min. See Table 3 for the summary of glass transition data shown in Figure 9.)

resulting in an average copolymer composition that is 54 mol % S and 46 mol % HS. (See Table 3 for T_g characterization of each S/HS random copolymer blend.) The DSC heat curves and derivative heat curves for two blend sets are shown in Figure 9. The 50/50 w/w SranHS19 and SranHS88 blend yields two distinct, sharp T_gs from scans associated with the second heat and the third heat (after 180 min annealing at 220 °C), with no apparent interphase T_g. Each T_g in the blend retains its position and breadth after long-term, high-temperature annealing, consistent with the existence of phase-separated domains of each random copolymer. (See the Supporting Information for T_g data

Table 3. Summary of Glass Transition Temperature Data (± 0.5 °C) for Figure 9

blend components	DSC curve	T_0 (°C)	T_e (°C)	T_{peak} (°C)[a]	ΔT_g (°C)
SranHS19/SranHS88	**a** (2nd heat)	103.0	119.1	111.8	16.1
		173.2	187.9	181.2	14.7
	b (3rd heat)	104.4	120.3	113.1	15.9
		172.8	188.1	181.2	15.3
SranHS37/SranHS71	**c** (2nd heat)	112.6	129.1	121.8	16.5
		159.4	172.6	165.9	13.2
	d (3rd heat)	113.2	129.9	122.8	16.7
		157.2	172.8	165.9	15.6

[a] The peak temperature from derivatives of DSC heating curves.

of each S/HS random copolymer.) The 50/50 w/w SranHS37 and SranHS71 blend also shows two distinct, sharp T_gs. These results strongly indicate that the broadening of T_g in S/HS gradient copolymers does not originate from the effect of "mixing" different compositional elements from different S/HS gradient copolymers. Instead, the observed T_g response in the gradient copolymers involves microphase separation in which a S-rich region of a S/HS gradient copolymer is surrounded by S-rich regions of like composition of other gradient copolymers, a region of a S/HS gradient copolymer with roughly equal S and HS units is surrounded by similar regions of other gradient copolymers, and a HS region of a S/HS gradient copolymer is surrounded by HS-rich regions of like composition of other gradient copolymers.

The very broad T_g response in gradient copolymers made from comonomers with strongly repulsive interactions indicates that gradient copolymers may be suited for technological applications in sound and vibration damping. It is well-known that at high frequency the vibration damping abilities of a polymer are strongly coupled with the glass transition.[27,42,48−50] Various approaches have been used to adjust and broaden the glass transition response of polymers and thereby increase the temperature range over which they exhibit good damping characteristics. These include plasticization,[48] addition of fillers,[48] and the production of multicomponent polymers with nanoheteregeneous morphologies, such as interpenetrating polymer networks[48,50] or gradient blends.[42] In the case of nanoheterogeneous, multicomponent polymers, there are substantial interfacial regions providing for a breadth of T_g response that is commonly associated with good damping characteristics over a broad range of use temperatures. Given that our experimental results on S/HS gradient copolymers are consistent with sinusoidal composition profiles in the nanophase-separated state and given that the interfacial profiles and resulting T_g breadth may be controlled by chain length, choice of comonomers, and the composition gradient, we plan to investigate the damping characteristics of an array of gradient copolymers by dynamic mechanical analysis and related means in the near future.

Summary

Gradient and block copolymers containing styrene and 4-hydroxystyrene units, with strongly repulsive comonomer interactions, were synthesized by nitroxide-mediated controlled radical polymerization of styrene and 4-acetoxystyrene followed by hydrolysis to transform 4-acetoxystyrene to 4-hydroxystyrene units. The glass transition behaviors of S/AS and S/HS copolymers with cumulative S mole fractions ranging from 0.37 to 0.71 were characterized using DSC heat curves as well as the derivatives of DSC heat curves; the latter provided quantitative comparisons of the T_g breadths among the copolymers. A single, narrow T_g was observed in each random copolymer indicating the absence of an ordered structure or nanophase (or microphase) separation. Two distinct, narrow T_gs were obtained in the S/AS and S/HS block copolymers, consistent with well-developed ordered structures or nanophase separation comprised of nearly pure S and nearly pure AS or HS segments, with nearly negligible interphase regions yielding no signature of an intermediate T_g. Because of the continuously varying sequence distributions along their chains, S/HS gradient copolymers exhibited remarkably large T_g breadths, ∼65−80 °C, approaching but not equaling the T_g difference between PS and PHS. Because the T_g difference between PS and PAS is much smaller than that between PS and PHS, the T_g breadths observed in S/AS gradient copolymers were only ∼25 °C.

The very broad T_g observed in the S/HS gradient copolymers is consistent with the presence of a sinusoidally varying composition profile[27] in the ordered state of the gradient copolymers. Furthermore, as determined by experiments in which the T_g behaviors of partial gradient copolymers (obtained from aliquots taken during gradient copolymerization) were compared to the full gradient copolymers (in which the composition varied along the chain from nearly pure S (or HS) to heavily HS (or S)), the T_g breadth was observed to grow continuously with increasing composition change in the S/HS gradient copolymers. This result is also consistent with the presence of a sinusoidally varying composition profile in the ordered state of gradient copolymers. The T_g breadth obtained in S/HS gradient copolymers cannot be reproduced by blending two S/HS random copolymers; instead, the blends exhibit two narrow T_gs indicative of phase separation between the random copolymers. The uniquely broad T_g response of gradient copolymers as compared with random and block copolymers containing strongly repulsive comonomers suggests that gradient copolymers may have technological utility in damping applications, where broad, continuous T_g behavior is a highly desired feature.

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Supporting Information Available: Procedures and characterization results for S/AS random and gradient copolymers synthesized in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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