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Syntheses of nanophase-segregated poly(vinyl acetate)–poly(dimethylsiloxane) and poly(vinyl acetate)–poly(styrene) graft copolymers

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Abstract

Graft copolymers with poly(vinyl acetate) (PVAc) backbones and poly(dimethylsiloxane) (PDMS) or poly(styrene) (PS) branches have been synthesized and their bulk nanophase-separation behaviors characterized. The PDMS and PS branches were prepared by anionic polymerization of hexamethylcyclotrisiloxane (D3) and styrene, respectively, followed by termination with chlorodimethylvinylsilane. Radical copolymerization of vinyl acetate with the vinyl terminus of these macromonomers yielded the PVAc-*g*-PDMS (**1**) and PVAc-*g*-PS (**2a–d**) graft copolymers. The branch repeat units of the copolymers were varied between 19 and 41 mol%. The graft copolymers were predicted to be moderately to strongly nanophase-segregated systems at room temperature by estimating the Flory–Huggins interaction parameters (χ) for the polymer segments. Thermal analyses revealed two glass transition temperatures for the PVAc and PDMS or PS polymer segments of the annealed samples, indicating that the polymer segments were locally phase-separated in the bulk phase. Transmission electron micrographs confirmed the presence of nanophase-separated PDMS- or PS-rich domains imbedded in a PVAc matrix.

Keywords: Poly(vinyl acetate); Poly(dimethylsiloxane); Poly(styrene)

1. Introduction

Graft copolymers with a backbone of one polymer and branches of another polymer exhibit material properties that are a combination of both homopolymer constituents (for reviews of graft copolymers, see Refs. [1–4]). Because of their physical properties, homopolymers of poly(vinyl acetate) (PVAc), poly(dimethylsiloxane) (PDMS), and poly(styrene) (PS) are important commercial plastics and are attractive candidates as components for syntheses of graft copolymers. For example, PVAc adheres well to many types of surfaces, forms tough and rigid films, is hydrophilic and exhibits good optical clarity [5]. Also, PVAc is useful in the preparation of inorganic–organic hybrid materials, because it forms homogeneous films during sol–gel curing [6]. PDMS is hydrophobic, highly flexible at room temperature, and exhibits low surface tension as a film [7]. PDMS has been used in a variety of applications, because of its biocompatibility and selective gas permeability. PS exhibits high thermal stability, has a high elastic modulus and is hydrophobic [8]. Graft copolymers with PVAc backbones and PDMS (PVAc-*g*-PDMS) or PS (PVAc-*g*-PS) branches (Fig. 1) are expected to exhibit some of the desirable characteristics of the individual component polymers, particularly if local phase separation of the backbone and graft branches can occur. There are several promising applications for mesoscopically ordered graft copolymers with PVAc backbones and with PDMS and PS branches, particularly as membranes for gas or solution separations [9].

Graft copolymers consist of homopolymers linked by covalent bonds, and these polymer segments can nanophase-separate in the bulk [2]. Experimental evidence and theoretical predictions indicate that thermodynamic considerations relating to polymer–polymer interactions in

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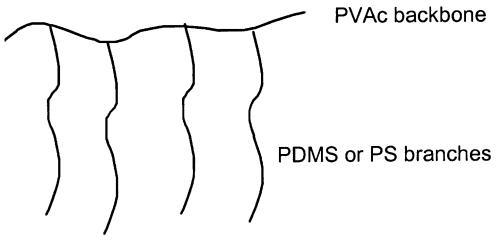

Fig. 1. Schematic diagram of a graft copolymer structure with a PVAc backbone and either PDMS or PS branches.

graft systems are analogous to those governing mesostructural ordering in diblock copolymers, although there are some differences imparted by the branched graft architecture [10–20]. The propensity for different component polymers in block copolymers to nanophase-separate at a certain volume fraction of the component polymers can be estimated by calculating χN, where χ is the segment–segment (Flory–Huggins) interaction parameter and N the degree of polymerization for the entire diblock copolymer. Diblock copolymers in the strong segregation limit ($\chi N > 100$) exhibit nanophase separation with well-developed nanodomain structures and narrow interphases, while copolymers in the weak/intermediate segregation regime ($20 > \chi N < 100$) tend to nanophase-separate with relatively broad interface regions (for a review of the bulk phase behavior of block copolymers, see Refs. [21,22]). For graft copolymers, the number and placement of the branches must also be considered, and it has been proposed that the number of branches per graft structure be included to predict whether the polymer will nanophase-separate at room temperature [18]. Consequently, component segregation in graft systems is estimated by calculating, $\chi N/\lambda$, where λ is the number of branches per graft copolymer, instead of χN. For example, in the case of graft copolymers with random placements of a large number (>30) of branches along the backbone and equal volume fractions of backbone and branch segments, values of $\chi N/\lambda > 100$ are anticipated to lead to strong nanophase separation [18]. This can be used as a guide for selecting graft copolymer compositions and architectures that may be expected to undergo bulk nanophase separation.

Graft copolymers with PVAc backbones and PDMS and PS branches have been previously synthesized by Tezuka and coworkers [23,24] using the macromonomer method, where the branch segments with vinyl end groups are formed first and then copolymerized with vinyl acetate (VAc) to form the graft copolymers (for a review of the macromonomer method, see Ref. [25]). However, these copolymers were synthesized as precursors to poly(vinyl alcohol) backbone graft copolymers and the properties, particularly the bulk phase behaviors, of the PVAc backbone graft systems were not examined. Here, we describe the synthesis and characterization of graft copolymers with PVAc backbones and PDMS or PS branches with systematically varied compositions. The extents of local phase separation of the polymers at room temperature were estimated by calculating $\chi N/\lambda$ for the copolymers, and measured experimentally by differential scanning calorimetry (DSC) thermal analysis and transmission electron microscopy (TEM).

2. Experimental

2.1. Reagents

Hexamethylcyclotrisiloxane (D3, TCI), was stirred for 2 days over CaH_2 at 70°C and bulb-to-bulb distilled under an argon atmosphere. Styrene (Aldrich) was washed with a 5 wt% sodium hydroxide solution to remove the inhibitor, dried with $CaCl_2$, filtered, stirred over CaH_2 and distilled immediately before use. VAc (Aldrich) was fractionally distilled immediately before use. Azobis(2-methylpropionitrile) (AIBN) was recrystallized from ethanol. Tetrahydrofuran (THF) was distilled from CaH_2, refluxed over sodium/benzophenone and distilled immediately before use. Toluene was refluxed over CaH_2, distilled, refluxed over sodium and distilled directly into the reaction flask. Benzene and ethyl acetate were stirred over CaH_2 for 2 days, distilled and kept under an argon atmosphere until use. *sec*-Butyl lithium (1.3 M in cyclohexane) and chlorodimethylvinylsilane were purchased from Aldrich and used as received.

2.2. Poly(dimethylsiloxane) macromonomer

A 250 ml round-bottom flask with a side-arm equipped with a 14/20 female joint and stopcock was flame-dried under vacuum and purged with argon five times. D3 (7.74 g, 0.035 mol) and 200 ml of THF were distilled directly into the flask. Under argon, the reaction mixture was cooled to 0°C, and *sec*-butyl lithium (0.7 ml, 0.97 mmol) was added via syringe before the reaction mixture was slowly warmed to room temperature. The reaction was stirred for 100 min at room temperature, after which time chlorodimethylvinylsilane (1.34 ml, 9.67 mmol) was added and the mixture was stirred for an additional 8 h. The THF was removed in vacuo, and toluene and sodium carbonate were added until the polymer dissolved. The resulting solution was precipitated into a 10-fold excess of methanol, centrifuged to isolate the polymer, and dried at 50°C under vacuum for several days to yield 5.32 g (68.7%) of the product as a clear oil. ^{1}H NMR: δ (ppm) 0.075 (s, 6H). IR: 2963.1, 1260.8, 1091.5, 1089.6, 1071.3, 1067.4, 1065.5, 1062.6, 1059.7, 1020.7 and 797.4 cm^{-1}.

2.3. Poly(styrene) macromonomer

Styrene (17.3 g, 0.17 mol) was anionically polymerized following the procedure of Gottschalk and Schmidt [26]. The polymerization was then terminated after 1 h with chlorodimethylvinylsilane (1.9 ml, 13.6 mmol). The mixture was allowed to warm to room temperature and stirred for

8 h. The reaction mixture was precipitated into a 10-fold excess of methanol, filtered, washed with methanol and dried at 30–40°C under vacuum. The polymer was subsequently freeze-dried from benzene to yield 14.6 g (84.4%) of the product as a white solid. ^{1}H NMR: δ (ppm) 7.09 (bm, 3H), 6.50 (bm, 2H), 1.84 (bm, 1H) and 1.43 (bm, 2H). IR: 3081.7, 3060.1, 3025.8, 2924.6, 2923.6, 2848.9, 1601.1, 1492.6, 1452.2, 757.4, 755.5 and 697.6 cm^{-1}.

2.4. Poly(vinyl acetate)-g-poly(dimethylsiloxane) (**1**)

The PVAc-*g*-PDMS graft copolymer was synthesized following the procedure of Tezuka et al. [23]. An additional purification step was performed to remove excess macromonomer, where the copolymer was subjected to Soxhlet extraction with hexanes and dried under vacuum at 70°C for several days to yield 37% of the product as a white solid. ^{1}H NMR: δ (ppm) 4.85 (bm, 1H), 2.00 (bm, 3H), 1.74 (bm, 2H) and 0.037 (s, 6H). IR: 2963.1, 1739.0, 1436.7, 1373.6, 1258.3, 1241.0, 1095.0, 1021.6 and 801.8 cm^{-1}.

2.5. Poly(vinyl acetate)-g-poly(styrene) (**2a**–**d**)

The PVAc-*g*-PS graft copolymers were synthesized following a literature procedure [24]. The yields were between 27 and 37%, and the products were white powders. ^{1}H NMR: δ (ppm) 7.12 (bm, 3H), 6.52 (bm, 2H), 4.88 (bm, 1H), 2.02 (bm, 3H), 1.78 (bm, 2H + 1H) and 1.44 (bm, 2H). IR: 3060.5, 3025.8, 3000.8, 2969.4, 2959.8, 2924.6, 1738.1, 1452.2, 1438.2, 1428.5, 1372.1, 1242.9, 1121.4, 1064.5, 1022.7, 756.5 and 698.6 cm^{-1}.

2.6. Characterization

Macromonomer branch precursors and graft copolymer products were characterized by ^{1}H NMR spectroscopy using a Varian Gemini 200 NMR spectrometer operating at 200.13 MHz. The ^{1}H NMR repetition delays used for the macromonomers and graft copolymers were 1.5 and 30 s, respectively. End group analyses were conducted on a General Electric GN-500 NMR spectrometer operating at 500.13 MHz in double precision mode. $CDCl_3$ was used as the solvent in all cases, and the ^{1}H NMR peaks were referenced to those in tetramethylsilane. Infrared spectra were acquired using a Mattson Galaxy Series FTIR 3000 spectrometer by casting thin polymer films onto a NaCl plate. Gel permeation chromatography (GPC) measurements were made on a Hewlett Packard Ti Series 1050 GPC with a Polymer Laboratories crosslinked-polystyrene column and refractometer detector. In each case, the solvent was ethyl acetate, the flow marker was toluene and the calibration standards were polystyrenes with narrow molecular weight distributions. The viscosity-average molecular weight was determined from a solution of polymer dissolved in toluene at 35°C using a Cannon Ubbelohde Viscometer (size #50). The viscometer was calibrated against pure toluene, and the K and a values[4] used were 12.5×10^{-3} ml g^{-1} and 0.703, respectively [27]. Glass transition, crystallization and melting temperatures of the polymers were determined to an accuracy of ±0.5°C using a Perkin–Elmer 7 Series Unix DSC7 differential scanning calorimeter (DSC) for temperature scans above 0°C and a Mettler TA 3000 DSC for temperature scans below 0°C. In both cases, an indium calibration standard was used and the scanning speeds of the heating and cooling cycles were 10°C min^{-1}. Samples were annealed to reduce kinetic influences on nanophase separation by dissolving the polymers in chloroform and allowing the solvent to evaporate slowly over 1 week, followed by heating at 125°C for 1 h and then at 110°C for 24 h. TEM was performed on annealed samples that were microtomed at −130°C (PVAc-*g*-PDMS, **1**) and room temperature (PVAc-*g*-PS, **2a**) using a diamond knife with a Reichert Ultracuts Microtome. The film thicknesses were 80 and 50 nm, respectively. For the PVAc-*g*-PS sample (**2a**), the PS regions were selectively stained by exposure to a ruthenium tetraoxide (RuO_4) water solution (0.5%). Staining was not required for the PVAC-*g*-PDMS sample (**1**). Images were recorded on a JEOL 1210 transmission electron microscope using an accelerating voltage of 120 kV.

3. Results and discussion

3.1. Macromonomer syntheses

The end group of the macromonomers must react with VAc, because the macromonomers will be radically copolymerized with VAc. Assuming that the polymer chain does not hinder reactivity, the macromonomer reactivity can be correlated with the end group reactivity [25]. Trimethylvinylsilane and VAc have comparable reactivity ratios of 0.85 and 0.38, respectively (reactivity ratios were calculated using data from Ref. [28]) so that the relative fractions of these monomers incorporated into the graft copolymers are expected to correspond approximately to the amount of the respective monomer in the feed [29]. Dimethylvinylsilane is closely related to trimethylvinylsilane and was selected as the end group moiety for the macromonomers. PDMS and PS with vinyl end groups were synthesized by anionic polymerization of D3 or styrene using *sec*-butyl lithium as an initiator, followed by termination with chlorodimethylvinylsilane to form the macromonomers (Fig. 2). In both cases, vinylation of the end groups was complete, as measured by ^{1}H NMR spectroscopy.

The molecular weights determined for the PDMS and PS macromonomers were 6500 g mol^{-1} (viscosity-average molecular weight, M_v) and 9000 g mol^{-1} (number-average molecular weight, M_n), respectively. M_n was determined from GPC measurements calibrated against polystyrene

[4] Both K and a are constants associated with the Mark–Houwink–Sakurada equation, $\nu = KM_v^a$, where ν is the intrinsic viscosity and M_v the viscosity-average molecular weight of the polymer.

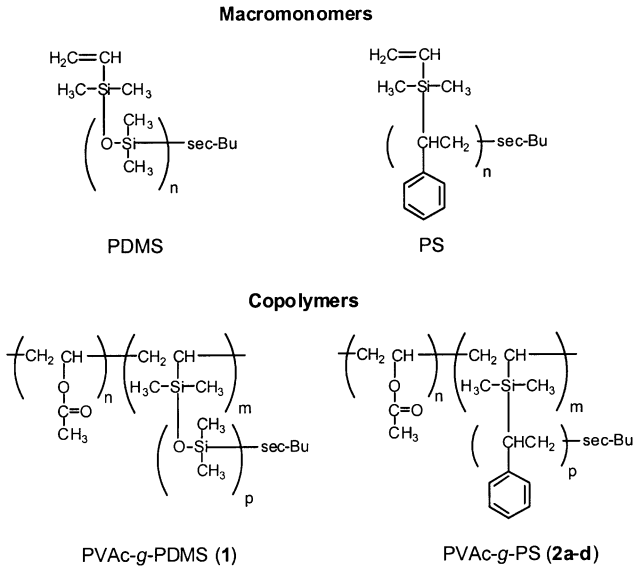

Fig. 2. Structures of the PDMS and PS macromonomers and PVAc-*g*-PDMS (**1**) and PVAc-*g*-PS (**2a**–**d**) graft copolymers.

standards, and so was accurate for the PS macromonomer. For the PDMS macromonomer, GPC calibration standards for PDMS were not available, so the viscosity-average molecular weight was determined instead. In this case, M_v was more accurate than M_n, because the former could be calculated from the PDMS intrinsic viscosity using constants specific for PDMS. The polydispersity index (PDI) was determined from GPC to be 1.13 for both polymers. In both cases, the measured molecular weights of the products were higher than the expected molecular weights (4000 g mol^{-1} for PDMS and 7400 g mol^{-1} for PS) based on the initial monomer-to-initiator ratios [29]. Because the polystyrene macromonomer was prepared under nominally living conditions, the discrepancy in molecular weight is likely due to impurities in the monomer or the solvent. These would scavenge some of the *sec*-butyl lithium initiator and lead to a higher molecular weight product [26]. In the case of PDMS, the polymerization is not living because of end group back-biting and reshuffling reactions, so the molecular weight cannot be accurately estimated by the monomer-to-initiator ratio [27,30]. While these side-reactions tend to broaden the molecular weight distribution, a narrow polydispersity (1.13) was obtained for PDMS by halting the reaction prior to completion [27,30].

3.2. Graft copolymer syntheses

The PDMS and PS macromonomers (Fig. 2) were copolymerized with VAc in benzene using AIBN as an initiator to yield PVAc-*g*-PDMS (**1**) and PVAc-*g*-PS (**2a**–**d**) graft copolymer products. The feed and final copolymer compositions associated with the preparations of products **1** and **2a**–**d** are shown in Table 1. For copolymer **1**, the target mole percent of DMS repeat units was 35%, the feed mole percent was 41% DMS and the mole percent of DMS in the final PVAc-*g*-PDMS product was 20%, as determined by ^{1}H NMR. This corresponds to an average number of three PDMS branches attached to each PVAc backbone. The DMS product composition in the graft copolymer was less than expected and attempts to increase the amount of DMS per copolymer by increasing the mole percent in the feed did not result in the incorporation of more DMS in the final graft products. This has been previously observed [23] and is thought to be due to macrophase separation of the copolymer and macromonomer during copolymerization.

For the PVAc-*g*-PS copolymers, a range of compositions were obtained, depending on the concentration of the polystyrene macromonomer initially present. For total mole percents of styrene repeat units of 15, 25, 35 and 45% in the reaction mixture, the resultant mole percents of styrene repeats in the graft copolymer products **2a**–**d** were 19, 27, 41 and 39%, respectively, as determined by ^{1}H NMR. This corresponds to average numbers of PS chains incorporated per graft copolymer of 1.1, 2.0, 1.9 and 2.8 for the respective PVAc-*g*-PS products, which have different molecular weights (see Table 1). The concentrations of styrene repeat units in the final products appear to be roughly proportional to the concentrations initially present in the feed. In this case, the PS polymer chains do not significantly alter the reactivity of the dimethylvinylsilane end groups with VAc.

Table 1
Composition and molecular weight data for PVAc-*g*-PDMS (**1**) and PVAc-*g*-PS (**2a**–**d**) copolymers (copolymerization of the PDMS or PS macromonomers with VAc in benzene was undertaken using AIBN as an initiator)

Sample	Target mol%, repeat unit	Feed mol%, repeat unit	Feed mol%, macromonomer	Total mol%, copolymer[a]	Average no. of branches per copolymer	M_n ($\times 10^{-4}$)[b]	PDI[b]
1	35	41	0.79	20	3.0	9.48	1.42
2a	15	15	0.20	19	1.1	4.96	1.46
2b	25	25	0.38	27	2.0	6.62	1.46
2c	35	35	0.62	41	1.9	4.07	1.52
2d	45	45	0.94	39	2.8	6.38	1.60

[a] Calculated from the ^{1}H NMR specta.
[b] Determined by GPC with polystyrene calibration standards and ethyl acetate as the eluent.

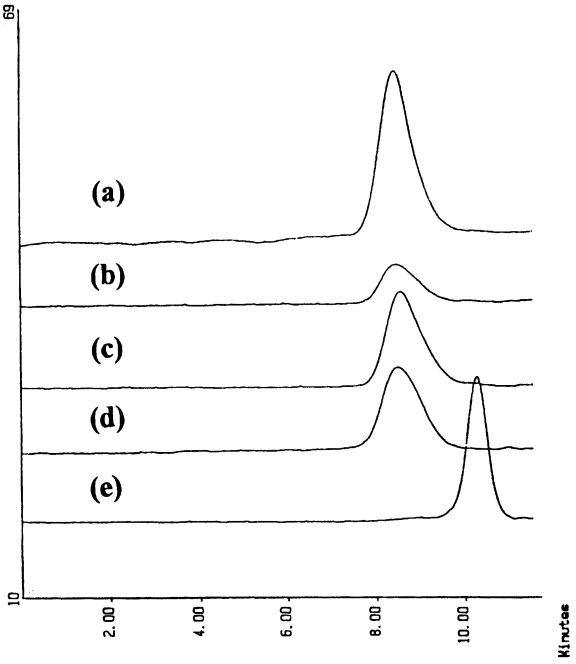

Fig. 3. GPC traces for PVAc-*g*-PS copolymers samples: (a) **2a**; (b) **2b**; (c) **2c**; (d) **2d**; (e) PS macromonomer.

The number-average molecular weight (M_n) and PDI values for the graft copolymers were determined by GPC against polystyrene standards (Table 1). The PDMS branch product **1** had a M_n of 94,800 g mol^{-1}, while the PS-branch copolymers **2a**–**d** had M_n values between 72,300 and 102,000 g mol^{-1}. The PDI values were between 1.42 and 1.60. For copolymers synthesized by the macromonomer technique, the difficulty of removing unreacted macromonomer from the final graft copolymers makes it important to determine copolymer purity, which was assessed using GPC. As shown in Fig. 3, the GPC traces for copolymers **2a**–**d** reveal single peaks that correspond to the graft products, with no evidence of PS macromonomer species. These results establish that the macromonomer was completely removed (within the sensitivity limits of the method) from each of the product graft copolymers. The same was observed for the PVAc-*g*-PDMS graft copolymer (**1**).

3.3. Nanophase separation

It has been hypothesized that graft copolymers with random placements of 1–3 graft branches along the backbone will locally phase-separate, depending on $\chi N/\lambda$ and the volume fractions of the component polymers [18]. For the PVAc-*g*-PDMS and PVAc-*g*-PS graft copolymers, $\chi N/\lambda$ values were calculated to predict the extents of nanophase separation of the polymer segments at room temperature. Because the χ parameters are not experimentally known for these systems, values of χ were estimated from the polymer solubility parameters and molar volumes according to Eq. (1):

$$\chi = \frac{V_0(\delta_2 - \delta_1)^2}{k_b T}, \quad (1)$$

where V_0 is the molar volume, δ_1 and δ_2 the solubility parameters of the respective polymer components, k_b the Boltzmann constant and T the temperature [31]. The molar volume, V_0, was calculated from the molar volumes of the respective monomers, V_1 and V_2, using $V_0 = (V_1 V_2)^{1/2}$, and the solubility parameters were calculated from the cohesive energies of the polymer segments, E_{coh}, using $\delta = (E_{coh}/V)^{1/2}$.[5] For the PVAc/PDMS and PVAc/PS systems, χ/T values were estimated to be $18.2/T$ and $68.9/T$ K^{-1}, respectively. Values for N were calculated using $N = N_{PVAc} + \lambda N_{PDMS}$ or $N_{PVAc} + \lambda N_{PS}$ and experimentally determined mean values for the number of branches, λ. These results for the PVAc-*g*-PDMS (**1**) and PVAc-*g*-PS (**2a**–**d**) graft systems are tabulated in Table 2. Of principal interest are the $\chi N/\lambda$ values estimated for graft copolymers **1** and **2b**–**d**, which have $\chi N/\lambda$ values of 35–85 in the weakly to moderately segregated regime. This indicates that these bulk systems may be expected to display nanophase separation at room temperature, though with some mixing of the copolymer components at their interfaces with each other. PVAc-*g*-PS graft copolymer **2a** has a larger $\chi N/\lambda$ value of 117, which indicates the likelihood of nanophase separation with relatively sharp interfaces between the components at room temperature.

Table 2
Estimation of $\chi N/\lambda$ values for the PVAc-PDMS and PVAc-PS graft copolymers

Sample	χ/T (K^{-1})[a]	Total MW ($\times 10^4$)	N	λ	$\chi N/\lambda$[b]
PVAc-*g*-PDMS, **1**	$18.2/T$	9.48	1138	3.0	35
PVAc-*g*-PS, **2a**	$68.9/T$	4.96	557	1.1	117
PVAc-*g*-PS, **2b**	$68.9/T$	6.62	733	2.0	85
PVAc-*g*-PS, **2c**	$68.9/T$	4.07	439	1.9	54
PVAc-*g*-PS, **2d**	$68.9/T$	6.38	691	2.8	57

[a] Estimated from polymer solubility parameters and molar volumes, see Footnote 5.
[b] Calculated for $T = 298$ K.

The extents of nanophase separation in the PVAc-*g*-PDMS and PVAC-*g*-PS graft copolymers have been characterized experimentally by DSC, TEM and X-ray diffraction. Bulk DSC measurements examine the characteristic thermal signatures of phase and glass transitions in the different materials, which reflect the degrees of local component segregation. DSC results for the macromonomers and graft copolymer products **1** and **2a**–**d** are

[5] The solubility parameter for PDMS was calculated by applying the additivity principle to the group cohesive energies and molar volumes. For PS and PVAc, the solubility parameters and molar volumes were known. The cohesive energies, molar volumes, solubility parameters and molar volumes were taken from Ref. [31].

Table 3
Thermal analyses of macromonomers and graft copolymers (temperatures ±0.5°C were determined by DSC analysis at 10°C min^{-1}; data are reported for the second heating of the samples. Samples were annealed at 125°C for 1 h, followed by 110°C for 24 h)

Sample	T_{g1} (°C)	T_{g2} (°C)	T_c (°C)	T_m (°C)
PDMS macromonomer	−128.0		−84.5	−47.5, −35
PS macromonomer		93.5		
PVAc-*g*-PDMS, **1**	−134.0	34.0	−104.0	−48.0
PVAc-*g*-PS, **2a**	42.5	94.0		
PVAc-*g*-PS, **2b**	41.0	94.0		
PVAc-*g*-PS, **2c**	41.5	92.0		
PVAc-*g*-PS, **2d**	39.5	88.0		

summarized in Table 3, with several representative DSC traces shown in Fig. 4. The PDMS macromonomer exhibited thermal behavior that is typical for PDMS polymers [32], possessing a glass transition temperature (T_g) at −128.0°C, a crystallization temperature (T_c) at −84.5°C, and bimodal melting temperatures at (T_{m1}) −47.5°C and (T_{m2}) −35.0°C. The PS macromonomer had a glass transition temperature of 93.5°C, consistent with published values for polystyrene in the literature [33]. PVAc has a T_g reported to be between 24 and 39°C [34].

The annealed sample of graft copolymer PVAc-*g*-PDMS (**1**) exhibited two glass transitions at temperatures of −134.0 and 34.0°C, corresponding to the PDMS and PVAc moieties, respectively.[6] Detection of glass transition temperatures associated with each of the respective homopolymers indicates that the PDMS branches and PVAc backbone segments in this sample are locally separated into distinct regions. These results are corroborated by the TEM image in Fig. 5, which shows nanosegregated regions of dark PDMS segments and lighter PVAc. Separate small-angle X-ray scattering (SAXS) measurements (not shown here) reveal an intense reflection at $q = 0.025$, corresponding to a *d*-spacing of 25 nm. The DSC measurements also registered a single melting temperature for the PDMS segments at −48.0°C (see Table 3), instead of the bimodal melting observed for the PDMS macromonomer. Furthermore, crystallization of the PDMS segments was detected at −104.0°C, significantly lower than observed for the PDMS macromonomer (−84.5°C). These results suggest that, after annealing, the PDMS and PVAc polymer segments remain partially mixed at their mutual interface regions [35]. Collectively, these results are consistent with the weakly-to-moderately nanophase-separated structure predicted by value of $\chi N/\lambda$ (35) calculated for this PVAc-*g*-PDMS graft copolymer (see Table 2).

Similar results were obtained from the analyses of PVAc-*g*-PS graft copolymers **2a**–**d**. As shown in Fig. 4, DSC

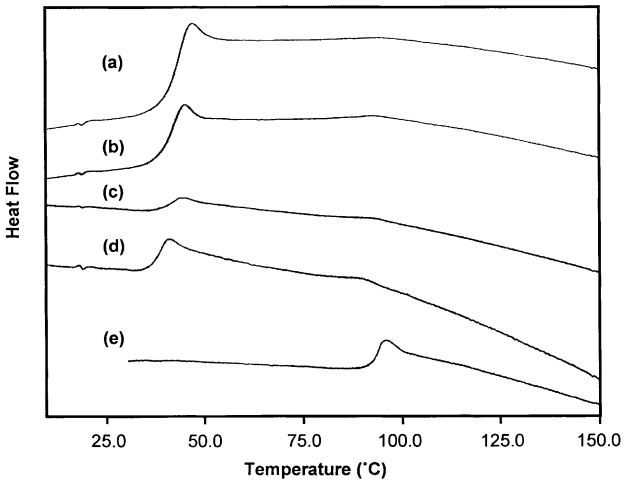

Fig. 4. Thermograms from DSC analyses of PVAc-*g*-PS copolymers samples: (a) **2a**; (b) **2b**; (c) **2c**; (d) **2d**; (e) PS macromonomer.

measurements performed on annealed PVAc-*g*-PS graft copolymers exhibited two glass transition temperatures in the ranges of 39.5–42.5 and 88.0–94.0°C (Table 3), corresponding to nanophase separation of the PVAc and PS segments, respectively.[6] Fig. 6 shows a representative TEM micrograph obtained from sample **2c**, in which dark-stained regions of PS are nanoscopically segregated from lighter appearing PVAc. SAXS measurements also support such nanophase separation, yielding intense reflections that indicate ordering length scales of ca. 25 nm in the different PVAc-*g*-PS samples. The T_g values (Table 3) associated

Fig. 5. TEM image of PVAc-*g*-PDMS graft copolymer **1** with dark PDMS-rich domains imbedded in the lighter PVAc matrix. The scale bar represents 100 nm.

[6] The samples were annealed for 1 h at 125°C, followed by 24 h at 110°C. In all cases, as observed by thermal analysis, the annealed samples demonstrated higher extents of local component separation than the unannealed samples.

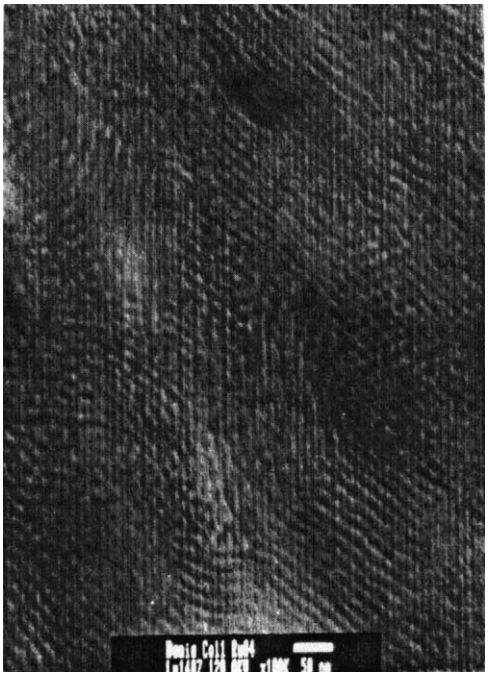

Fig. 6. TEM image of PVAc-*g*-PS graft copolymer **2c** with dark PS-rich domains imbedded in the lighter PVAc matrix. The scale bar represents 50 nm.

with the PVAc segments are all somewhat higher than expected for neat PVAc (24–39°C), which may reflect partial mixing of PVAc and PS segments at their interfaces. Again, this is consistent with $\chi N/\lambda$ values for graft copolymers **2b**–**d**. (54–85, Table 2), which anticipate moderate nanophase separation. Such mixing reflects somewhat weaker local phase segregation than predicted for product **2a**. However, as stated previously, the approximate $\chi N/\lambda$ values represent estimates of the copolymer segment compatibilities. The DSC, TEM and XRD results are consistent with the theoretically estimated extents of nanoscopic ordering in the PVAc-*g*-PS systems.

4. Conclusions

PVAc-*g*-PDMS and PVAc-*g*-PS graft copolymers have been synthesized by the macromonomer technique with 1–3 graft branches and branch repeat units varying between 19 and 41 mol% in the final products. Intermediate nanophase separations were generally predicted by $\chi N/\lambda$ values that were calculated for each graft copolymer composition. Thermal analyses and TEM corroborated these predictions and showed that the PVAc–PDMS or PVAc–PS segments were locally separated in the bulk graft copolymer samples. This leads to insights that can be incorporated into the rational design of branched copolymers with nanophase-separated PVAc backbones and PDMS or PS grafts. Such graft copolymers and others that nanophase segregate may be useful for a variety of different uses, depending on the component polymers and structural ordering. In particular, these hydrophilic–hydrophobic graft copolymer systems may be useful in membrane applications or as precursors for sol–gel-derived mesostructured composites.

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References

[1] Dreyfuss P, Quirk RP. In: Mark HF, Bikales NM, Overberger CC, Menges G, Kroschwitz JI, editors. 2nd ed. Encyclopedia of polymer science and engineering, vol. 7. New York: Wiley/Interscience, 1987. p. 551–79.
[2] Pitsikalis M, Pispas S, Mays JW, Hadjichristidis N. Adv Polym Sci 1998;135:1–137.
[3] Ito K, Kawaguchi S. Adv Polym Sci 1999;142:129–78.
[4] Burchard W. Adv Polym Sci 1999;143:113–94.
[5] Daniels W. In: Mark HF, Bikales NM, Overberger CC, Menges G, Kroschwitz JI, editors. 2nd ed. Encyclopedia of polymer science and engineering, vol. 17. New York: Wiley/Interscience, 1987. p. 393–425.
[6] Girard-Reydet E, Lam TM, Pacault JP. Macromol Chem Phys 1994;195:149–58.
[7] Simionescu BG, Harabagiu V, Simionescu CI. In: Salamone JC, editor. Polymer materials encyclopedia, vol. 10. Boca Raton, FL: CRC Press, 1997. p. 7751–8.
[8] Hahnfeld JL, Dalke BD. In: Mark HF, Bikales NM, Overberger CC, Menges G, Kroschwitz JI, editors. 2nd ed. Encyclopedia of polymer science and engineering, vol. 16. New York: Wiley/Interscience, 1987. p. 62–71.
[9] Miyata T, Takagi T, Uragami T. Macromolecules 1996;29:7778–94 (and references therein).
[10] Floudas G, Hadjichristidis N, Iatrou H, Pakula T, Fischer EW. Macromolecules 1996;27:7735–46.
[11] Pochan DJ, Gido SP, Pispas S, Mays JW, Ryan AJ, Fairclough JPA, Hamley IW, Terrill NJ. Macromolecules 1996;29:5091–8.
[12] Pochan DJ, Gido SP, Pispas S, Mays JW. Macromolecules 1996;29:5099–105.
[13] Gido SP, Lee C, Pochan DJ, Pispas S, Mays JW, Hadjichristidis N. Macromolecules 1996;29:7022–8.
[14] Xenidou M, Beyer FL, Hadjichristidis N, Gidos SP, Beck Tan N. Macromolecules 1998;31:7659–67.
[15] Lee C, Gido SP, Poulos Y, Hadjichristidis N, Beck Tan N, Trevino SF, Mays JW. Polymer 1998;39:4631–8.
[16] Beyer FL, Gido SP, Büschl C, Iatrou H, Uhrig D, Mays JW, Ying Chang M, Garetz BA, Balsara NP, Beck Tan N, Hadjichristidis N. Macromolecules 2000;33:2039–48.
[17] Olvera de la Cruz M, Sanchez IC. Macromolecules 1986;19:2501–8.
[18] Shinozaki A, Jasnow D, Balazs AC. Macromolecules 1994;27:2496–502.
[19] Foster DP, Jasnow D, Balazs AC. Macromolecules 1995;28:3450–62.
[20] Gido SP, Wang Z-G. Macromolecules 1997;30:6771–82.
[21] Bates FS, Fredrickson GH. Annu Rev Phys Chem 1990;41:525–57.

[22] Bates FS. Science 1991;251:898–905.
[23] Tezuka Y, Fukushima A, Imai K. Makromol Chem 1985;186:685–94.
[24] Tezuka Y, Araki A. Makromol Chem 1993;194:2827–37.
[25] Ito K. Prog Polym Sci 1998;23:581–620.
[26] Gottschalk A, Schmidt H-W. Liq Cryst 1989;5:1619–27.
[27] Zilliox JG, Roovers JEL, Bywater S. Macromolecules 1975;8:573–8.
[28] Greenley RZ. In: Brandruk J, Immergut EH, editors. Polymer handbook, 3rd ed. New York: Wiley/Interscience, 1989. p. II/267–74.
[29] Odian G. Principles of polymerization. 3rd ed. New York: Wiley/Interscience, 1991.
[30] Gnanou Y, Rempp P. Makromol Chem 1988;189:1997–2005.
[31] Van Krevelen DW, Hoftyzer PJ. Properties of polymers their estimation and correlation with chemical structure. New York: Elsevier, 1976.
[32] Bordeaux D, Cohen-Addad JP. Polymer 1990;31:743–8.
[33] Rudd JF. In: Brandruk J, Immergut EH, editors. Polymer handbook, 3rd ed.. New York: Wiley/Interscience, 1989. p. V/82.
[34] Lindemann MK. In: Brandruk J, Immergut EH, editors. Polymer handbook, 3rd ed. New York: Wiley/Interscience, 1989. p. V/72.
[35] Smith SD, DeSimone JM, Huang H, York G, Dwight DW, Wilkes GL, McGrath JE. Macromolecules 1992;25:2575–81.