

Origin of the Difference in Order–Disorder Transition Temperature between Polystyrene-*block*-poly(2-vinylpyridine) and Polystyrene-*block*-poly(4-vinylpyridine) Copolymers

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ABSTRACT: Three polystyrene-*block*-poly(2-vinylpyridine) (S2VP diblock) and three polystyrene-*block*-poly(4-vinylpyridine) (S4VP diblock) copolymers with varying molecular weights and block compositions were synthesized via anionic polymerization, and their order–disorder transition temperatures (T_{ODT} s) were determined using oscillatory shear rheometry and small-angle X-ray scattering (SAXS). It has been found that for comparable molecular weight and block composition the T_{ODT} of S4VP diblock copolymer is exceedingly high compared with that of S2VP diblock copolymer. The experimental observation has been confirmed by theoretical predictions from currently held mean-field theory. For the theoretical predictions, temperature-dependent interaction parameters for the polystyrene (PS)/poly(2-vinylpyridine) (P2VP) pair and the PS/poly(4-vinylpyridine) (P4VP) pair were determined from SAXS profiles obtained at varying temperatures ranging from 125 to 185 °C for a low-molecular-weight (LMW) S2VP diblock copolymer and ranging from 160 to 195 °C for an LMW S4VP diblock copolymer and curve fitting to the Leibler theory. The molecular weights of LMW S2VP and LMW S4VP diblock copolymers employed were 10 200 and 2720, respectively, enabling us to obtain SAXS profiles in the disordered state of the respective block copolymers. The temperature-dependent specific volumes of PS, P2VP, and P4VP were determined at temperatures ranging from 25 to 200 °C using spectroscopic ellipsometry. To find the origin of the experimentally observed difference in T_{ODT} between S2VP and S4VP diblock copolymers, the thermally stimulated current method and dielectric relaxation spectroscopy were employed to investigate differences in polarizability between S2VP and S4VP diblock copolymers. It is concluded that much higher T_{ODT} of S4VP diblock copolymers as compared with the T_{ODT} of S2VP diblock copolymers is attributable to the stronger polarizability of P4VP in S4VP diblock copolymer compared with the polarizability of P2VP in S2VP diblock copolymer.

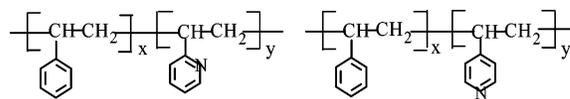
1. Introduction

In the past two decades, a very large number of papers have been published reporting on order–disorder transition (ODT) in microphase-separated block copolymers. There are too many to cite them all here, and interested readers are referred to some review articles.^{1,2} Among the many block copolymers investigated, diene-based block copolymers, namely polystyrene-*block*-polyisoprene (SI diblock) copolymer, polystyrene-*block*-polybutadiene (SB diblock) copolymer, polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymer, and polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS triblock) copolymer, were employed extensively.

Confining our attention to SI and SB diblock copolymers, it has been reported^{3,4} that the ODT temperatures (T_{ODT} s) of an SI diblock copolymer having predominantly vinyl microstructures in PI block or an SB diblock copolymer having predominantly vinyl microstructure in PB block are much higher than those of SI or SB diblock copolymers having predominantly 1,4-addition of PI block or 1,4-addition of PB block. That is,

the microstructures of the polydiene block in SI or SB diblock copolymers have a profound influence on their T_{ODT} s. It is well established today that one can synthesize SI or SB diblock copolymers having predominantly 1,4-addition of isoprene in PI block or predominantly 1,4-addition of butadiene in PB block using cyclohexane as a solvent and SI or SB diblock copolymers having predominantly vinyl microstructures (e.g., ~60% 3,4-addition and ~35% 1,2-addition) of isoprene in PI block or predominantly 1,2-addition (over 90%) of butadiene in PB block using tetrahydrofuran as a solvent.⁵

When synthesizing vinylpyridine-containing diblock copolymers, one can have polystyrene-*block*-poly(2-vinylpyridine) (S2VP diblock) copolymer or polystyrene-*block*-poly(4-vinylpyridine) (S4VP diblock) copolymer, the only difference between the two lying in the position of the nitrogen atom in the pyridine ring, as illustrated below.



PS-*block*-P2VP Copolymer

PS-*block*-P4VP Copolymer

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Table 1. Molecular Characteristics of S2VP and S4VP Diblock Copolymers Synthesized in This Study

sample code	M_w (g/mol)	M_n (g/mol)	w_{PS} (wt frac)	$T_{g,PVP}$ (°C)	T_{ODT} (°C)
S2VP-LMW	10 200 ^a	8 870	0.46		disordered
S2VP-1	21 260 ^a	20 170	0.37	99.0	179
S2VP-2	18 100 ^a	17 470	0.50	100.0	156
S2VP-3	19 890 ^a	19 020	0.65	100.0	disordered
S4VP-LMW	2 720 ^b	2 310	0.50		disordered
S4VP-1	15 560	13 490 ^c	0.35	146.4	>300
S4VP-2	16 930	14 300 ^c	0.50	146.4	>300
S4VP-3	51 350	39 220 ^c	0.65	146.4	>300

^a GPC-MALLS was used. ^b MALDI-TOF was used. ^c NMR was used to determine M_n , and then M_w was calculated using the value of M_w/M_n determined using SEC in DMF against P2VP standards.

Earlier, Schulz et al.⁶ reported on the T_{ODT} of S2VP diblock copolymers of relatively low molecular weights ($\sim 20\,000$) with varying block compositions. Today, it is well established that block composition affects both the T_{ODT} and the microdomain structure of block copolymers.^{7,8} It has long been recognized that 4-vinylpyridine has higher dipole moment than 2-vinylpyridine.⁹ It is then reasonable to speculate that the position of the nitrogen atom, whether in 2- or 4- in the pyridine ring, in a vinylpyridine block may influence the T_{ODT} of the corresponding block copolymers. Recently, Lee et al.¹⁰ reported that the increment in the domain spacing of S2VP diblock copolymer with cadmium chloride ($CdCl_2$) is much larger than that of S4VP diblock copolymer. To our knowledge, however, no study has ever been reported on a comparison of T_{ODT} between S2VP and S4VP diblock copolymers. Such an investigation can have significant implications in the synthesis of functional block copolymers containing poly(vinylpyridine) block.

Very recently, we synthesized a series of S2VP and S4VP diblock copolymers with varying molecular weights and block compositions and then measured their T_{ODTs} using oscillatory shear rheometry and small-angle X-ray scattering (SAXS). We have found that for comparable molecular weight and block composition the T_{ODT} of S4VP diblock copolymer is exceedingly high compared with that of S2VP diblock copolymer. To confirm the experimental observations, we determined the temperature-dependent segmental interaction parameter $\alpha(T)$ for the polystyrene (PS)/poly(2-vinylpyridine) (P2VP) pair and the PS/poly(4-vinylpyridine) (P4VP) pair, respectively, by curve fitting the SAXS profiles, which were obtained at temperatures in the disordered state of low-molecular-weight S2VP and S4VP diblock copolymers, to the Leibler theory.⁷ Using the $\alpha(T)$ determined, we estimated the T_{ODTs} of the S2VP and S4VP diblock copolymers synthesized in this study using currently held mean-field theory.^{7,8} We confirmed the experimental observation of very large difference in T_{ODT} between S2VP and S4VP diblock copolymers. In order to explain the physical origin of the large difference in T_{ODT} between S2VP and S4VP diblock copolymers that were observed experimentally, we employed thermally stimulated currents (TSC) method^{11–14} and dielectric relaxation spectroscopy (DRS)^{15,16} to S2VP and S4VP diblock copolymers. Both the TSC method and DRS employed revealed that the polarizability of S4VP diblock copolymer is greater than that of S2VP diblock copolymer. On the basis of the above observations, we have concluded that the unusually large difference in T_{ODT} between S2VP and S4VP diblock copolymers is attributable to the difference in polarizability between S2VP and S4VP diblock copolymers. In this paper we present the highlights of our findings.

2. Experimental Section

Synthesis and Characterization of Polymers. In this study, we synthesized, via sequential anionic polymerization, three S2VP diblock copolymers and three S4VP diblock copolymers in tetra-

hydrofuran (THF) at $-78\text{ }^\circ\text{C}$ using *sec*-butyllithium as initiator. To determine the weight-average molecular weight (M_w) and polydispersity index (PDI) of S2VP diblock copolymers, we employed size exclusion chromatography (SEC, Waters 1525) coupled with a multiangle laser light scattering (MALLS) device (PD2020, Precision Detector). For the measurement, a polymer sample was dissolved in THF (0.5 mg/cm^3), and the solution was filtered using a syringe filter with pore size of $0.2\text{ }\mu\text{m}$. In so doing, a small amount (5 mmol/L) of LiCl was added to THF to preclude possible adsorption of P2VP block in the columns. When the molecular weight of an S2VP diblock copolymer was lower than about $20\,000$, nuclear magnetic resonance (NMR) spectroscopy (Varian 300 MHz) was also employed to determine the number-average molecular weight (M_n), for which the ratio of a peak position (ppm) corresponding to *sec*-butylene initiator and a peak position (ppm) corresponding to phenyl and pyridine rings was used. The M_w and PDI of S4VP diblock copolymers were determined using matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Reflex III) when the molecular weight of an S4VP diblock copolymer was lower than ~ 8000 . For the experiment, a polymer sample was first dissolved in chloroform (1.0 mg/cm^3). The solution was placed in a sample holder, and the solvent was removed completely at room temperature. When the molecular weight of an S4VP diblock copolymer was higher than about 8000 , we employed NMR and SEC against P2VP standards. For the measurements, dimethylformamide (DMF) was used as a solvent. Table 1 gives a summary of the molecular weights, block composition as determined by NMR spectroscopy, and glass transition temperature ($T_{g,PVP}$) as determined by differential scanning calorimetry (DSC) of the P2VP phase in each S2VP diblock copolymer or of the P4VP phase in each S4VP diblock copolymer. It should be mentioned that the glass transition temperature of the polystyrene phase ($T_{g,PS}$) overlapped the $T_{g,PVP}$ in the S2VP diblock copolymers, and the $T_{g,PS}$ in each S4VP diblock copolymer was $\sim 100\text{ }^\circ\text{C}$. Also given in Table 1 are the molecular weights of two additional low-molecular-weight (LMW) S2VP and S4VP diblock copolymers, designated as S2VP-LMW and S4VP-LMW, which were used to conduct SAXS experiments to determine temperature-dependent interaction parameter, the results of which will be presented later in this paper. For such purposes, the molecular weight of the polymer had to be sufficiently low, enabling us to conduct SAXS experiments in the disordered state of each block copolymer.

Oscillatory Shear Rheometry. An Advanced Rheometric Expansion System (ARES, TA Instruments) was used in the oscillatory mode with a parallel plate fixture (8 mm diameter). Dynamic temperature sweep experiments under isochronal conditions were conducted; i.e., the dynamic storage modulus (G') and dynamic loss modulus (G'') were measured at an angular frequency (ω) of 0.01 or 0.1 rad/s during heating. We also conducted dynamic frequency sweep experiments using a parallel plate fixture (8 mm diameter), measuring G' and G'' as functions of ω (ranging from 0.01 to 100 rad/s) at various temperatures between 120 and $190\text{ }^\circ\text{C}$, for which a fixed strain of 0.04 was used to ensure that measurements were taken well within the linear viscoelastic range of the materials investigated. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within $\pm 1\text{ }^\circ\text{C}$. All experi-

ments were conducted under a nitrogen atmosphere to preclude oxidative degradation of the samples.

Small-Angle X-ray Scattering (SAXS). In this study, synchrotron SAXS measurements were performed on beamline 4C1 at the Pohang Light Source (Republic of Korea) where W/B4C double multilayer monochromator delivered monochromatic X-rays with a wavelength (λ) of 0.1608 nm and a resolution $\Delta\lambda/\lambda \approx 0.01$ onto the sample. A two-dimensional CCD camera (Princeton Instruments, SCX-TE/CCD-1242) was used to collect the scattered X-rays. For the SAXS experiments, S2VP diblock copolymer samples were annealed at 120 °C for 48 h under vacuum, and S4VP diblock copolymer samples were annealed at 180 °C for 48 h under vacuum. The sample thickness was 1 mm. For the low-molecular-weight diblock copolymers, S2VP-LMW and S4VP-LMW, the absolute values of scattered X-ray intensity were collected at various temperatures with an exposure time of 150 s for S2VP-LMW and 400 s for S4VP-LMW.

Transmission Electron Microscopy (TEM). TEM images of specimens were taken at room temperature after a specimen was rapidly quenched from an elevated temperature to ice water. The ultrathin sectioning (50–70 nm) was performed by ultramicrotomy at room temperature for an S2VP diblock copolymer stained with iodine at room temperature using a Reichert Ultracut E sectioning system. A transmission electron microscope (JEM1200EX 11, JEOL) operated at 120 kV was used to obtain images of block copolymer specimens.

Measurement of Temperature-Dependent Specific Volume. In this study, we needed information on the temperature-dependent specific volumes of three homopolymers, PS, P2VP, and P4VP, in order to obtain expressions, via SAXS, for the temperature-dependent interaction parameters for PS/P2VP and PS/P4VP pairs. Later in this paper, we will present a mathematical expression that contains a term requiring information on the specific volumes of PS and P2VP for an S2VP diblock copolymer and the specific volumes of PS and P4VP for an S4VP diblock copolymer. The densities of homopolymers, PS, P2VP, and P4VP, at room temperature were measured using a density meter (LC-P, Mettler Toledo). The densities of PS, P2VP, and P4VP were found to be 1.05, 1.14, and 1.11 g/cm³, respectively. For the measurements of specific volume at elevated temperatures, samples were prepared using the following procedures. A thin film of PS ($M_w = 3.8 \times 10^5$ purchased from Aldrich Chemical) was prepared by spin-coating at a rate of 4000 rpm from 5 wt % toluene solution in PS on a passivated silicone wafer, where the oxide layer was removed using 5% aqueous solution of hydrofluoric acid followed by annealing at 120 °C for 24 h. The film thickness after the complete removal of the toluene was found to be 362 nm. A thin film of P2VP ($M_w = 4.5 \times 10^4$ synthesized in our laboratory) was prepared by spin-coating at a rate of 4000 rpm from *n*-butanol solution (5 wt % in P2VP) on a silicone wafer followed by annealing at 120 °C for 24 h. The film thickness after the complete removal of the solvent was found to be 146 nm. A thin film of P4VP ($M_w = 1.6 \times 10^5$ purchased from Aldrich Chemical) was prepared by spin-coating at a rate of 2000 rpm from DMF solution (5 wt % in P4VP) on a silicone wafer followed by annealing at 180 °C for 24 h. The film thickness after the complete removal of the DMF was found to be 145 nm.

The specific volumes of PS, P2VP, and P4VP at elevated temperatures were determined from the measurements of changes in film thickness with increasing temperature using spectroscopic ellipsometry (J.A. Woollam) at an incidence angle of 75°. The measurement was carried out upon heating from 25 to 200 °C at a heating rate of 2 °C/min. Because of the very small thickness of the film compared with the surface area of the film (~10 cm²), the change in film thickness ($\Delta H/H_0$) with temperature was assumed to be the same as the change in volume ($\Delta V/V_0$) with temperature, where H_0 and V_0 respectively are the thickness and the volume of the film at 25 °C.

Thermally Stimulated Current (TSC) Method. The TSC method has long been used to characterize dielectric relaxation phenomenon in polymers. There are numerous references available

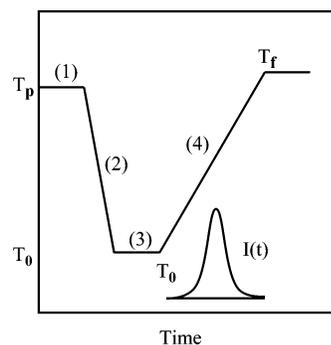


Figure 1. Schematic showing the polarization process during TSC experiment: step 1 denotes the polarization process at a temperature T_p ; step 2 denotes a rapid cooling from T_p to a very low-temperature T_0 , which is far below the glass transition temperature T_g of the specimen; step 3 denotes the period of rest at T_0 with the polarization voltage switched off; step 4 denotes the heating process at a constant rate from T_0 to the final temperature T_f , which is higher than T_p .

on this method, and the readers are referred to only some selected references.^{11–14} In the present study, we obtained TSC spectra of P2VP, P4VP, S2VP diblock copolymer, and S4VP diblock copolymer using a thermally stimulated current spectrometer (Setaram TSC-II, France) after poling a sample placed in the chamber of the spectrometer. To facilitate the discussion of our experimental results presented below, let us look at the schematic, shown in Figure 1, describing the polarization procedure employed. Basically, a dielectric sample is placed between two electrodes maintained at a fixed distance and polarized by applying an electric field at a polarization temperature (T_p) above its glass transition temperature (T_g) (usually 3–5 °C above T_g) so that polarization attains equilibrium with the applied field (step 1). After that, the sample is cooled down, with the electric field turned on, to a temperature T_0 well below its T_g (say to $T_g - 100$ K), such that the polarization of the sample is frozen (step 2). The polarization voltage is then turned off for a predetermined period, and thus the sample is kept at the state of frozen-in polarization (step 3). The depolarization current, while returning to equilibrium of dipolar units, is then measured with the aid of an electrometer as the temperature is increased from T_0 to a predetermined temperature T_f , which is higher than the T_p , at a constant heating rate (step 4), resulting in a TSC spectrum shown in the inset of Figure 1. By integrating the depolarization current at time, $I(t)$, with respect to time over which TSC measurements were conducted, we obtain remanent polarization (P_r) defined by

$$P_r = \frac{1}{A} \int I(t) dt \quad (1)$$

where A is the area of a sample, I is the current, and t is the time.^{12,15} In the present study, a sample of polymer film was mounted on an electrode of the TSC sample cell and poled at a predetermined condition. A dc electric field of about 3–6 MV/m was applied at a T_p for a predetermined period (20 min).¹⁷ After poling, the thermally stimulated depolarization currents were measured as a function of temperature while the poled sample was being heated through its T_g at a heating rate of 7 °C/min. The remanent polarization P_r defined by eq 1, which is equal to the charge per unit area, was calculated.

Dielectric Relaxation Spectroscopy (DRS). Dielectric relaxation spectroscopy (DRS) has long been used to investigate the motions of permanent dipoles and free charges of polymers, and today DRS is well recognized as a very useful experimental technique to probe the segmental motions of polymers and even to investigate the miscibility of polymer blends. There are too many references to cite them all here, and therefore the readers are referred to only a few references describing the principles and applications of DRS.^{15,16} In the present study, we conducted frequency (ω) sweep of dielectric complex permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) of P2VP, P4VP,

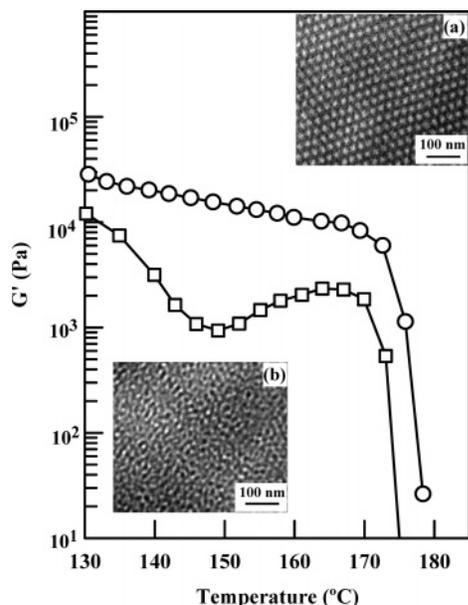


Figure 2. Effect of thermal history of S2VP-1 on the variations of dynamic storage modulus G' with temperature during isochronal dynamic temperature sweep experiment at an angular frequency of 0.01 rad/s: (\square) annealed at 120 °C for 48 h and (\circ) annealed at 160 °C for 48 h. Inset (a) gives a TEM image of the specimen, which had been annealed at 160 °C for 48 h and quenched rapidly from 160 °C to ice water, and inset (b) gives a TEM image of the specimen, which had been annealed at 120 °C for 48 h and quenched rapidly from 120 °C to ice water.

S2VP diblock copolymer, and S4VP diblock copolymer over a wide range of ω ($1-10^6$ Hz) using a Novocontrol broadband dielectric converter and a Solatron SI 1260 impedance/gain-phase analyzer. For the experiments, polymer films of disk shape (10 mm in diameter) were employed. The dielectric constants (ϵ') of P2VP, P4VP, S2VP diblock copolymer, and S4VP diblock copolymer over a wide range of ω were compared, and the differences in ϵ' between S2VP and S4VP diblock copolymers were used to determine the differences in polarizability.

3. Results and Discussion

Order–Disorder Transition Temperature (T_{ODT}) of the S2VP and S4VP Diblock Copolymers. We employed both oscillatory shear rheometry and SAXS to determine the T_{ODTs} of the three S2VP diblock copolymers and three S4VP diblock copolymers synthesized in this study. Figure 2 shows variations of dynamic storage modulus (G') with temperature during the isochronal dynamic temperature sweep experiments at an angular frequency (ω) of 0.01 rad/s for two specimens of S2VP-1, one annealed at 120 °C for 48 h and another annealed at 160 °C for 48 h, in the heating process. Note that the weight fraction of PS block in S2VP-1 is 0.37 as determined by ^1H NMR spectroscopy (see Table 1). It is of great interest to observe in Figure 2 that the temperature dependence of G' during heating is quite different, depending on the thermal history of the specimens. If we did not conduct the dynamic temperature sweep experiment for the specimen that had been annealed at 160 °C for 48 h, we might have concluded that the specimen, which had been annealed at 120 °C for 48 h, underwent an order–order transition at a temperature of ~ 148 °C, where G' went through a minimum. However, as can be seen from Figure 2, a minimum in G' disappeared completely when a specimen had been annealed at 160 °C for 48 h. The insets in Figure 2 show TEM images of two specimens, which had received the same thermal treatments as the specimens that were employed for the dynamic temperature sweep experiments. The TEM

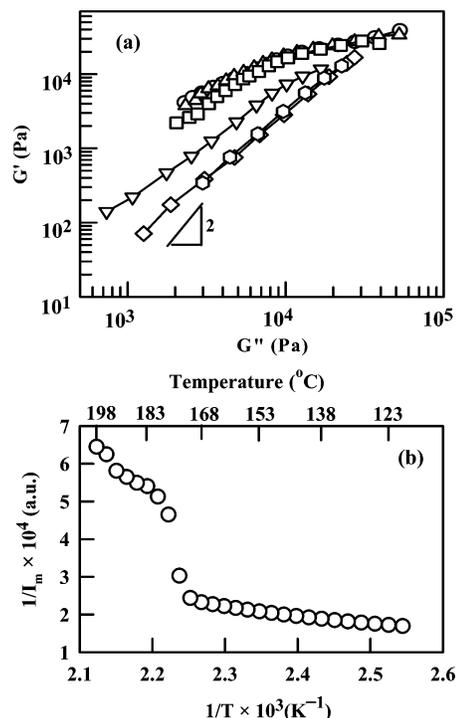


Figure 3. (a) Plots of $\log G'$ vs $\log G''$ for S2VP-1 obtained from the dynamic frequency sweep experiment during heating at various temperatures (°C): (\circ) 165, (Δ) 170, (\square) 173, (∇) 176, (\diamond) 179, and (\circ) 182. (b) Plots of $1/I_m$ vs $1/T$ for S2VP-1 obtained from SAXS experiment in the heating cycle. Prior to both experiments, specimens were annealed at 160 °C for 48 h.

image of the specimen (on the upper right side of Figure 2), which had been annealed at 160 °C for 48 h followed by a rapid quench into ice water, shows “gyroid” microdomains. This was confirmed by SAXS measurements (see the Supporting Information). On the other hand, from the TEM image of the specimen (on the lower left side in Figure 2), which had been annealed at 120 °C for 48 h followed by a rapid quench into ice water, we conclude that the block copolymer has ill-defined “bicontinuous” structure because our SAXS experiment indicates that the scattered intensity decreases with increasing temperature, indicating that microdomains existed at temperatures below a certain critical temperature. The details of the analysis of SAXS measurements of both specimens of S2VP-1 are presented in the Supporting Information. It is worth mentioning that the TEM image of a S2VP-1 specimen, which was annealed at 120 °C for 48 h, is very similar to the TEM image reported in Figure 8 of a paper by Court and Hashimoto,¹⁸ in which the authors investigated the morphology of a binary mixture of two SI diblock copolymers using both TEM and SAXS and concluded that the particular binary blend specimen had bicontinuous structure.

Figure 3a shows plots of $\log G'$ vs $\log G''$ for S2VP-1 obtained from the dynamic frequency sweep experiments during heating at various temperatures ranging from 165 to 182 °C. It is seen that $\log G'$ vs $\log G''$ plots begin to be independent of temperature with a slope very close to 2 at 179 °C and remain there at 182 °C. Following the rheological criterion of Han and co-workers,¹⁹ we determined the T_{ODT} of S2VP-1 to be about 179 °C. This value is in good agreement with the temperature (about 175 °C) at which values of G' begins to drop rapidly from the isochronal dynamic temperature sweep experiments shown in Figure 2. The determination of T_{ODT} of microphase-separated block copolymer from such a plot has been used for the past three decades since the seminal study of

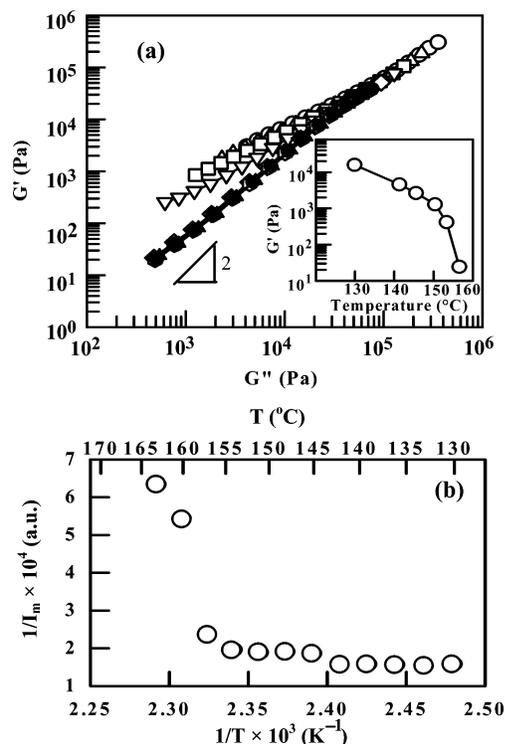


Figure 4. (a) Plots of $\log G'$ vs $\log G''$ for S2VP-2 obtained from the dynamic frequency sweep experiment during heating at various temperatures ($^{\circ}\text{C}$): (\circ) 140, (Δ) 145, (\square) 150, (∇) 153, (\diamond) 156, (\circ) 159, (\bullet) 162, and (\blacktriangle) 165. Inset shows variations of G' with temperature during the dynamic temperature sweep experiments at an angular frequency of 0.1 rad/s. (b) Plots of $1/I_m$ vs $1/T$ for S2VP-2 obtained from SAXS experiment in the heating cycle. Prior to both experiments, specimens were annealed at 120 $^{\circ}\text{C}$ for 48 h.

Guinlock and Porter.²⁰ Figure 3b shows plots of the reciprocal of the maximum scattered intensity ($1/I_m$) vs the reciprocal of absolute temperature ($1/T$) for S2VP-1 from SAXS experiments conducted at various temperatures. It can be seen from Figure 3b that values of $1/I_m$ have a sudden change at temperatures between 172 and 177 $^{\circ}\text{C}$, indicating that the T_{ODT} of S2VP-1 lies at 173–176 $^{\circ}\text{C}$, which is in good agreement with that determined from Figure 3a. For the past two decades, plots of $1/I_m$ vs $1/T$ have been used to determine the T_{ODT} of microphase-separated block copolymers. There are too many papers to cite them all here. Interested readers are referred to a few selected papers.^{21,22}

Figure 4a shows plots of $\log G'$ vs $\log G''$ at various temperatures ranging from 140 to 165 $^{\circ}\text{C}$ from the dynamic frequency sweep experiments and plots of G' vs temperature from the isochronal dynamic temperature sweep experiments (inset) for S2VP-2, and Figure 4b shows plots of $1/I_m$ vs $1/T$ from SAXS experiments at various temperatures for S2VP-2. All three different experimental methods indicate that the T_{ODT} of S2VP-2 is between 156 and 159 $^{\circ}\text{C}$. Note that the weight fraction of PS block in S2VP-2 is 0.5, indicating that it has lamellar microdomains.

Figure 5a shows plots of $\log G'$ vs $\log G''$ at various temperatures ranging from 130 to 145 $^{\circ}\text{C}$ from the dynamic frequency sweep experiments and plots of G' vs temperature from the isochronal dynamic temperature sweep experiments (inset) for S2VP-3, and Figure 5b shows plots of $1/I_m$ vs $1/T$ from SAXS experiments at various temperatures for S2VP-3. It is interesting to observe from Figure 5a that in the terminal region the $\log G'$ vs $\log G''$ plots have a slope of 2 and are

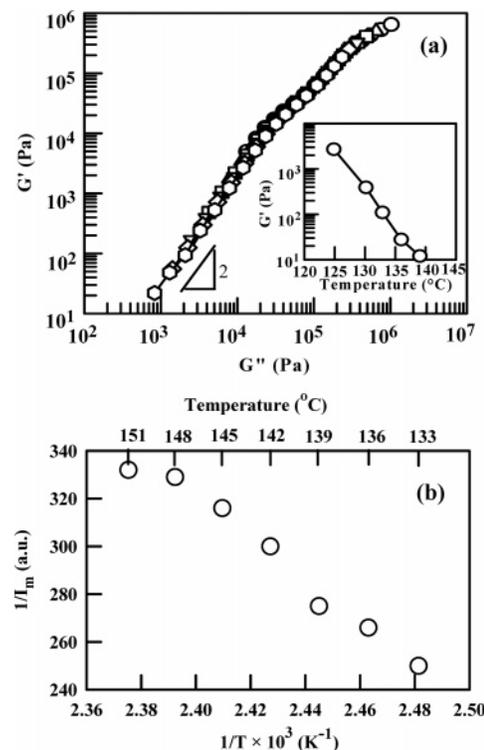


Figure 5. (a) Plots of $\log G'$ vs $\log G''$ for S2VP-3 obtained from the dynamic frequency sweep experiment during heating at various temperatures ($^{\circ}\text{C}$): (\circ) 130, (\square) 133, (Δ) 136, (∇) 139, (\diamond) 142, and (\circ) 145. Inset shows variations of G' with temperature during the dynamic temperature sweep experiments at an angular frequency of 0.1 rad/s. (b) Plots of $1/I_m$ vs $1/T$ for S2VP-3 obtained from SAXS experiment in the heating cycle. Prior to both experiments, specimens were annealed at 120 $^{\circ}\text{C}$ for 48 h.

independent of temperature over the entire of temperatures investigated, behavior observed in all monodisperse homopolymers, indicating that S2VP-3 is a disordered block copolymer. This conclusion is supported from the inset of Figure 5a in that values of G' steadily decrease with increasing temperature, behavior observed in all homopolymers. The same conclusion can be reached from Figure 5b in that values of $1/I_m$ increase (thus values of I_m decrease) steadily with increasing temperature.

Today, it is well established that the T_{ODT} of a block copolymer depends on the number of repeat units or degree of polymerization (N), block copolymer composition (f), and segmental interaction parameter χ (or α) between the constituent components. Notice in Table 1 that the molecular weights (or N) of the three S2VP diblock copolymers investigated in this study are not much different from each other. Therefore, the differences in T_{ODT} observed in Figures 3–5 are ascribed to the differences in the values of f among the three S2VP diblock copolymers.

Figure 6 shows variations of G' with temperature during the isochronal dynamic temperature sweep experiments at $\omega = 0.01$ rad/s for the three S4VP diblock copolymers synthesized in this study. It can be seen from Figure 6 that the T_{ODT} s of all three S4VP diblock copolymers exceed 300 $^{\circ}\text{C}$, the highest experimental temperature employed, although the molecular weight of S4VP-2, for example, is lower than that of S2VP-2, both having an identical value of f (see Table 1). In view of the fact that the T_{ODT} of a block copolymer depends on N , f , and χ (or α), it is then clear that differences in χ (or α) between S2VP and S4VP diblock copolymers should explain the exceedingly large differences in T_{ODT} between S2VP and S4VP diblock copolymers, observed experimentally in this study.

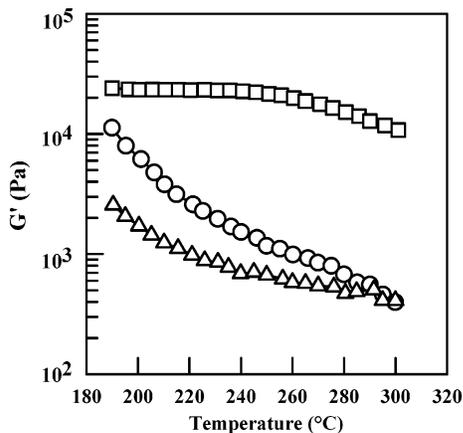


Figure 6. Variations of G' with temperature during the isochronal dynamic temperature sweep experiment at $\omega = 0.01$ rad/s for three S4VP diblock copolymers synthesized in this study: (○) S4VP-1, (△) S4VP-2, and (□) S4VP-3. Table 1 gives the molecular characteristics of the block polymers.

Temperature-Dependent Specific Volumes of PS, P2VP, and P4VP Determined from Spectroscopic Ellipsometry.

Using spectroscopic ellipsometry described in the Experimental Section, we determined the temperature-dependent specific volumes (v) of PS, P2VP, and P4VP. The specific volume of each homopolymer is plotted against temperature (in °C), as shown in Figure 7, in which we observe two distinct linear temperature dependencies, one below the T_g and another above the T_g of each homopolymer. Information on the temperature-dependent specific volume of each homopolymer is needed to determine the temperature-dependent segmental interaction parameters for PS/P2VP and PS/P4VP pairs from SAXS experiments, the details of which are described below. Further, the temperature-dependent specific volume of each homopolymer is needed to predict (or estimate) the T_{ODT} s of S2VP and S4VP diblock copolymers using currently held mean-field theory. For such purposes, we obtained, via regression analysis, the following expressions:

$$v_{PS} = 0.945 + 1.941 \times 10^{-4}(T - 273) \quad \text{for } T < 373 \text{ K} \quad (2)$$

$$v_{PS} = 0.905 + 6.076 \times 10^{-4}(T - 273) \quad \text{for } T > 373 \text{ K} \quad (3)$$

$$v_{P2VP} = 0.874 + 1.284 \times 10^{-4}(T - 273) \quad \text{for } T < 373 \text{ K} \quad (4)$$

$$v_{P2VP} = 0.852 + 3.752 \times 10^{-4}(T - 273) \quad \text{for } T > 373 \text{ K} \quad (5)$$

$$v_{P4VP} = 0.896 + 1.052 \times 10^{-4}(T - 273) \quad \text{for } T < 423 \text{ K} \quad (6)$$

$$v_{P4VP} = 0.851 + 4.174 \times 10^{-4}(T - 273) \quad \text{for } T > 423 \text{ K} \quad (7)$$

in which T denotes the absolute temperature.

Temperature-Dependent Segmental Interaction Parameters of S2VP and S4VP Diblock Copolymers Determined from SAXS. Figure 8 shows SAXS profiles at various temperatures in the disordered state of S2VP-LMW, and Figure 9 shows SAXS profiles at various temperatures in the disordered state of S4VP-LMW. Note that the absolute values of the

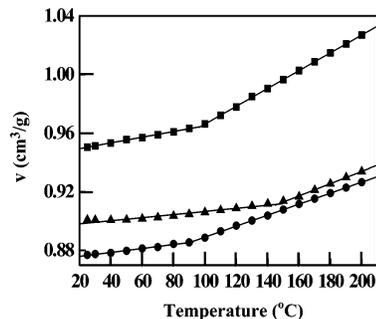


Figure 7. Temperature dependence of specific volumes for (●) P2VP, (▲) P4VP, and (■) PS, which were obtained in this study using spectroscopic ellipsometry.

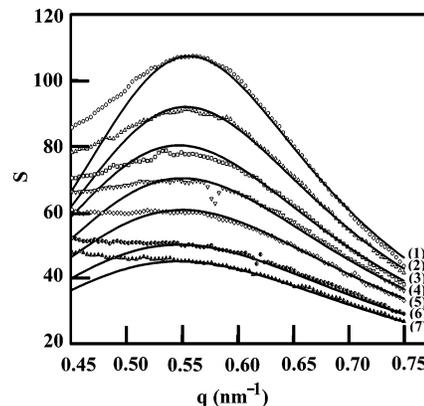


Figure 8. Temperature dependence of SAXS profiles for S2VP-LMW in the disordered state during the heating process at various temperatures (°C): (1) 130, (2) 140, (3) 150, (4) 160, (5) 170, (6) 180, and (7) 185. The solid lines are obtained by curve fitting SAXS profiles to eq 8.

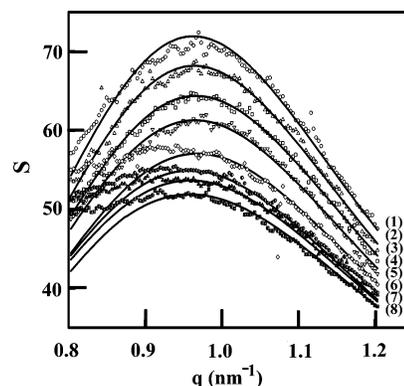


Figure 9. Temperature dependence of SAXS profiles for S4VP-LMW in the disordered state during the heating process at various temperatures (°C): (1) 160, (2) 165, (3) 170, (4) 175, (5) 180, (6) 185, (7) 190, and (8) 195. The solid lines are obtained by curve fitting SAXS profiles to eq 8.

dimensionless structure factor²³ S given in Figures 8 and 9 are obtained by $d\Sigma(q)/d\Omega$ (having the units of cm^{-1})

$$\frac{d\Sigma}{d\Omega} = \frac{KV_{\text{ref}}}{N_A} (a_1 - a_2)^2 S(q) \quad (8)$$

in which K is the machine constant (on the order of unity), V_{ref} is a reference molar volume, N_A is the Avogadro number, and a_i (having the units of cm^{-2}) for monomer i is defined by

$$a_i = \frac{N_A \rho_i Z_{e,i}}{[M]_{0,i}} r_e \quad (9)$$

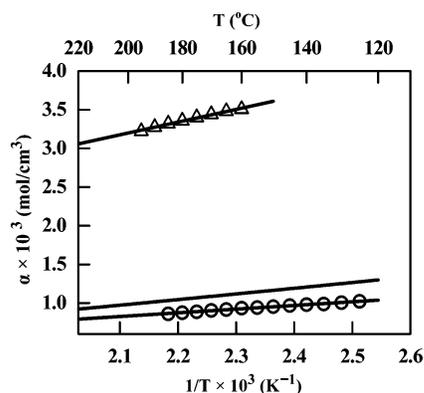


Figure 10. Plots of interaction parameter (α) vs the reciprocal of absolute temperature ($1/T$) and temperature (in $^{\circ}\text{C}$) for (O) S2VP-LMW and (Δ) S4VP-LMW, which were obtained from curve-fitting the SAXS profiles to the Leibler theory, eqs (8) and (9). For comparison, eq 15 for S2VP from Dai and Kramer²⁸ was used to draw the solid line.

where ρ_i , $Z_{e,i}$, and $[M]_{0,i}$ are the density, the total number of electrons, and the molecular weight of monomer i , respectively, and r_e is the electron radius (2.82×10^{-13} cm).

The dimensionless structure $S(q)$ for a diblock copolymer is given by⁷

$$S(q)^{-1} = \frac{F(x,f)}{N} - 2\chi \quad (10)$$

in which N is the total number of segments and given by V/V_{ref} in which V is the total molar volume of a block copolymer defined by $V = M_{w,1}v_1 + M_{w,2}v_2$ with $M_{w,i}$ and v_i being the weight-average molecular weight and the specific volume of block i , respectively, and χ is the Flory–Huggins interaction parameter. $F(x,f)$ appearing in eq 10 is defined by

$$F(x,f) = \frac{g(1,x)}{g(f,x)g(1-f,x) - \frac{1}{4}[g(1,x) - g(f,x) - g(1-f,x)]^2} \quad (11)$$

with $g(f,x)$ being the Debye function defined by

$$g(f,x) = 2[f x + \exp(-f x) - 1]/x^2 \quad (12)$$

in which x is defined by $x = R_g^2 q^2$ with R_g being the radius of gyration of an ideal (Gaussian) chain and q being the wave vector, and f is the volume fraction of PS block in an S2VP (or S4VP) diblock copolymer. Having obtained values of $d\Sigma(q)/d\Omega$ defined by eq 8, we determined values of χ (or $\alpha = \chi/V_{\text{ref}}$) from SAXS experiments at various temperatures in the disordered state of S2VP-LMW and S4VP-LMW, respectively.

Specifically, the value of χ (or α) at a given temperature was determined by curve fitting the experimentally obtained SAXS profiles, plot of $S(q)$ vs q , to eq 8 with the aid of eq 10. By repeating the same procedure at different temperatures for a given block copolymer (S2VP-LMW or S4VP-LMW), we prepared plots of α against the reciprocal of absolute temperature as given in Figure 10, from which we obtained the following expressions:

$$\alpha_{\text{PS/P2VP}} = -1.791 \times 10^{-4} + 0.478/T \quad (13)$$

for S2VP diblock copolymer and

$$\alpha_{\text{PS/P4VP}} = -1.370 \times 10^{-3} + 2.091/T \quad (14)$$

for S4VP diblock copolymer.²⁴ Note that α in eqs 13 and 14 has the units of mol/cm^3 . It can be seen from Figure 10 that values of α for S4VP diblock copolymer are much larger than those of S2VP diblock copolymer, and the temperature dependence of α is greater in S4VP diblock copolymer than in S2VP diblock copolymer. This observation has significant implications in that for comparable molecular weight and block copolymer composition the segregation power χN is much greater in S4VP diblock copolymer than in S2VP diblock copolymer, suggesting that the T_{ODT} of S4VP diblock copolymer is expected to be much higher than that of S2VP diblock copolymer. This is precisely what we have observed in this study.

It should be mentioned that Mori et al.²⁵ employed SAXS to determine temperature-dependent $\chi(T)$ for disordered SI diblock copolymers, while Bates and Hartney²⁶ employed small-angle neutron scattering (SANS) to determine the temperature-dependent $\chi(T)$ for disordered 1,4-polybutadiene-*block*-1,2-polybutadiene copolymers, and Russell et al.²⁷ also employed SANS to determine the temperature-dependent $\chi(T)$ for disordered polystyrene-*block*-poly(methyl methacrylate) copolymers. All three research groups employed the Leibler theory⁷ to determine $\chi(T)$. However, in their studies, constant values of specific volume v_i ($i = \text{A or B}$) for each block were used to determine $\chi(T)$ from eq 8 with the aid of eq 10.

Earlier, other research groups also made efforts to determine the temperature-dependent interaction parameter for S2VP or S4VP diblock copolymers. Specifically, Dai and Kramer²⁸ applied forward recoil spectrometry to a planar interface between homopolymer P2VP and blends of a homopolymer PS and a diblock copolymer consisting of deuterated PS block and P2VP block and obtained the following expression:

$$\chi = -0.033 + 66/T \quad (15)$$

Note that eq 15 was not obtained from neat S2VP diblock copolymer, as was done in this study and summarized by eq 13 for neat S2VP diblock copolymer. Nevertheless, for comparison, we can rewrite the temperature dependence of χ given by eq 15 in terms of α using the relationship between the two:

$$\alpha = (-0.033 + 66/T)/V_{\text{ref}} \quad (16)$$

in which V_{ref} is defined by

$$V_{\text{ref}} = [(v_{\text{PS}}M_{\text{S}})(v_{\text{P2VP}}M_{\text{VP}})]^{1/2} \quad (17)$$

where v_{PS} and v_{P2VP} are specific volumes of PS and P2VP, respectively, and M_{S} and M_{VP} are molecular weights of styrene and vinylpyridine, respectively. Equation 16 with the aid of eq 17 is plotted (solid line) in Figure 10. It should be mentioned that, in the calculations of V_{ref} from eq 17, eq 3 for v_{PS} and eq 5 for v_{P2VP} were used. It is seen in Figure 10 that values of α from eq 16 are slightly larger than those from eq 13 over a very wide range of temperatures (120–220 $^{\circ}\text{C}$), although the slope of the α vs $1/T$ plot (thus the term related to the enthalpy) is similar. The consequence of the differences between the two will be reflected in the predicted values of T_{ODT} of S2VP diblock copolymers, which are presented below.

Other investigators also reported on values of χ for S2VP diblock copolymer, PS/P2VP and/or PS/P4VP pairs. Specifically, Clarke et al.²⁹ determined χ for the PS/P4VP pair using three different methods: (1) by measuring the equilibrium micelle spacing of S4VP diblock copolymer with secondary ion mass spectrometry (SIMS) at 165 and 180 $^{\circ}\text{C}$, (2) by measuring the contact angle for droplets of PS on a thin film of P4VP at 183 $^{\circ}\text{C}$, and (3) by measuring the interfacial width of a PS/

Table 2. Comparison of Experimentally Determined T_{ODT} with Theoretical Predictions for the S2VP and S4VP Diblock Copolymers Synthesized in This Study

(a) S2VP Diblock Copolymers							
sample code	M_w (g/mol)	w_{PS} (wt frac)	measured T_{ODT} (°C)	predicted T_{ODT} (°C) from Helfand–Wasserman theory		predicted T_{ODT} (°C) from Leibler theory	
				eq 13	eq 16	eq 13	eq 16
S2VP-1	21 260	0.37	174	174	241	436	431
S2VP-2	18 100	0.50	154	152	221	384	397
S2VP-3	19 890	0.65	disordered	117	195	299	335

(b) S4VP Diblock Copolymers						
sample code	M_w (g/mol)	w_{PS} (wt frac)	measured T_{ODT} (°C)	predicted T_{ODT} (°C) from Helfand–Wasserman theory		predicted T_{ODT} (°C) from Leibler theory
				eq 14		eq 14
S4VP-1	15 560	0.35	>300	606		790
S4VP-2	16 930	0.50	>300	696		859
S4VP-3	51 350	0.65	>300	993		1067

P4VP bilayer with neutron reflectometry at 160 °C. The estimated values of χ varied very much with the experimental methods employed: (1) the SIMS method yielded χ values for S4VP diblock copolymer varying from 3.5 to 7.5, (2) the contact angle measurement yielded $\chi = 0.4$ for the PS/P4VP pair, and (3) the interface width measurement yielded $\chi = 1.0$ for the PS/P4VP pair.

Alberda van Ekenstein et al.³⁰ determined values of χ for the PS/P2VP pair from blends of poly(styrene-*ran*-2-vinylpyridine) and PS and values of χ for the PS/P4VP pair from blends of poly(styrene-*ran*-4-vinylpyridine) and PS, using a simplified theory for the phase behavior of blends of a random copolymer and a homopolymer. Their findings are summarized as follows: $0.09 < \chi_{PS/P2VP} \leq 0.11$ and $0.30 < \chi_{PS/P4VP} \leq 0.35$, without specifying the temperatures at which the above relationships were warranted. For comparison, we calculated values of $\chi_{PS/P2VP}$ from eqs 13 and 17 using the relationship $\chi_{PS/P2VP} = \alpha_{PS/P2VP} V_{ref}$ and obtained $0.087 < \chi_{PS/P2VP} < 0.101$ at temperatures between 125 and 185 °C and obtained $0.317 < \chi_{PS/P4VP} < 0.347$ from eq 14 at temperatures between 160 and 195 °C. The calculated values are very close to those given in ref 30 although ref 30 does not give the temperature dependence of χ . It is clear that values of $\chi_{PS/P4VP}$ are much larger than those of $\chi_{PS/P2VP}$ at comparable temperatures.

Comparison of Measured T_{ODT} with Prediction. In this study, we predicted (or estimated) the T_{ODT} s of the three S2VP diblock copolymers and three S4VP diblock copolymers synthesized in this study (see Table 1) using the Leibler theory⁷ and also the Helfand–Wasserman theory,⁸ for which we employed the temperature-dependent $\alpha(T)$ given by eqs 13 and 14, together with the temperature-dependent specific volumes of PS, P2VP, and P4VP given by eqs 3, 5, and 7. For comparison, we also used eq 15 to estimate the T_{ODT} s of three S2VP diblock copolymers.

Table 2 gives a summary of the estimated T_{ODT} s, together with experimental results, for three S2VP diblock copolymers and three S4VP diblock copolymers synthesized in this study. For the calculations we used the information on the molecular weights and block copolymer compositions given in Table 1. It should be mentioned that the estimated values of T_{ODT} given in Table 2 must be regarded as being qualitative. Our purpose was to obtain information on a qualitative trend in the values of T_{ODT} with regard to the differences between S2VP and S4VP diblock copolymers. For many reasons, the determination of the temperature-dependent interaction parameters $\alpha(T)$ given by eqs 13 and 14 were obtained, via SAXS, using fairly low-

molecular-weight S2VP and S4VP diblock copolymers, especially S4VP-LMW. The most compelling reason for having chosen such low molecular weights (see Table 1) was that in order to use the Leibler theory we had to conduct SAXS experiments in the disordered state of the block copolymers. It was our experience that for molecular weights of block copolymers higher than those of S2VP-LMW and S4VP-LMW given in Table 1 did not allow us to obtain sufficient number of data points in the disordered state. We are well aware of the fact that the segmental interaction parameter depends on the molecular weight of a block copolymer. For instance, extending the lattice cluster theory,^{31,32} Freed and co-workers^{33,34} have shown that polymerization index N must be included in the expression for χ when dealing with polymer pairs or block copolymers having finite molecular weights and presented the following expression

$$\chi = (a + b/N) + (c + d/N)/T \quad (18)$$

where a , b , c , and d are constants and T is the absolute temperature. Notice that eq 18 reduces to

$$\chi = a + c/T \quad (19)$$

for very large values of N . We have already indicated that we had practical difficulties with using S2VP and S4VP diblock copolymers having molecular weights higher than those given in Table 1. Therefore, eqs 13 and 14 must be regarded as being a gross approximation.

Nevertheless, we make some interesting observations from Table 2. (1) The predicted values of T_{ODT} s of three S4VP diblock copolymers are exceedingly high compared with those of three S2VP diblock copolymers, confirming our experimental results. This is expected from Figure 10 because eq 14 has much larger values of α (or χ) than eq 13. (2) The predicted values of T_{ODT} from the Leibler theory are very high compared to those from the Helfand–Wasserman theory. Earlier, similar observations were made for diene-based block copolymers by Han and co-workers.^{19b} (3) The predicted values of T_{ODT} s of three S2VP diblock copolymers based on eq 16 are larger than those based on eq 13. This is expected from Figure 10 because eq 16 has larger values of α (or χ) than eq 13. (4) The predicted values of T_{ODT} for S2VP-1 and S2VP-2 are very close to measured values, which however might be regarded as being fortuitous.

Origin of the Difference in T_{ODT} between S2VP and S4VP Diblock Copolymers. Having observed that the value of the segmental interaction parameter α (or χ) for S4VP diblock

copolymer is much larger than that for S2VP diblock copolymer, we must find the origin of the large differences in α (or χ) between S2VP and S4VP diblock copolymers. From the point of view of chemical structures or molecular conformations, the only difference between S2VP and S4VP diblock copolymers is the position of the nitrogen atom, either at 2- or 4- in the pyridine ring, in the poly(vinylpyridine) block.

Pyridine is known to be a highly polar molecule. Since the pyridine molecule is electrically unbalanced and the centers of positive and negative charges do not coincide, it tends to turn in the electric field. The effect is known as "dipole polarization". The dielectric constant of asymmetric molecules containing dipoles (polar molecules) depends on the extent of dipole polarization, which in turn depends on temperature. The higher the dipole polarization, the larger the dielectric constant will be. When dipoles are directly attached to the chain, their movements depend on the ability of chain segment to move. Thus, the dipole polarization effect will be much less below the glass transition temperature (T_g) than above it. Then, it can easily be surmised that on application of an electric field complete dipole orientation will not be possible because of spatial requirements imposed by the chain structure. Further, it is known that the dipole moment of 4-pyridine is higher than that of 2-pyridine,⁹ which is attributable to steric hindrance in 2-pyridine. It is then reasonable to expect that dipole polarization in P2VP will be lower, due to steric hindrance, than in P4VP.

Earlier, Agnew³⁵ reported that the steric hindrance of P2VP is much greater than that of P4VP. Later, Kuo et al.³⁶ investigated the influence of the position of the nitrogen atom in the pyridine ring (P2VP vs P4VP) on hydrogen bonding and miscibility with phenolic resin, and they concluded that the P4VP has a greater ability to form hydrogen bonds than P2VP with phenolic due to the presence of steric hindrance on the nitrogen atoms in P2VP.

In an effort for finding an origin(s) of our experimental results presented above, we conducted TSC and DRS experiments to determine difference in polarizability between P2VP and P4VP and between S2VP and S4VP diblock copolymers. Figure 11a shows the normalized TSC spectra of P4VP, S4VP, P2VP, and S2VP as a function of temperature (see Figure 1 for polarization procedure). Each polymer exhibits a strong relaxation peak at 97.3 °C for S2VP, 106.0 °C for P2VP, 135.4 °C for S4VP, and 137.5 °C for P4VP. Each relaxation peak represents the glass transition temperature (T_g) of the corresponding polymer. It can be seen in Figure 11a that the relaxation peak of S2VP copolymer appears at a temperature slightly lower than that of P2VP, which is attributable to the lower polarizability of the PS block in the S2VP diblock copolymer as compared with the polarizability of neat P2VP. The small relaxation peak appearing at a temperature near 70 °C in the TSC spectrum for the S2VP diblock copolymer (curve 3) is due to the presence of a PS block. Note that this relaxation peak will become more conspicuous when an S2VP diblock copolymer is poled at a temperature near the T_g of PS block. Notice in Figure 11a that the relaxation peak of P4VP appears at temperature much higher than that of P2VP, indicating that P4VP has a higher polarity than P2VP. It has been reported that the dipole moment of 4-pyridine is higher than 2-pyridine owing to steric hindrance in 2-pyridine.⁹ Referring to Figure 11a, we observe that the relaxation peak of P4VP is only slightly higher than that of S4VP, and the TSC spectrum for S4VP is much broader than that of P4VP. This observation is attributable to a broader molecular weight distribution (MWD) of S4VP, as compared with the MWD of P4VP, because the TSC spectrum for S4VP begins to increase

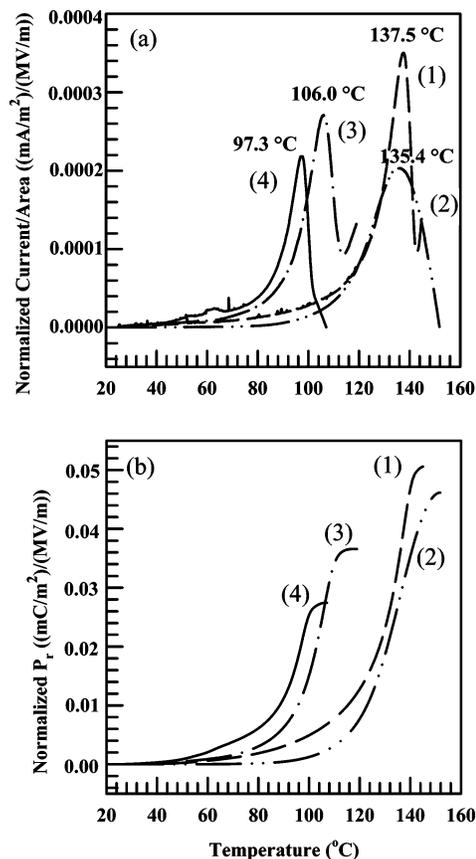


Figure 11. (a) Plots of normalized currents vs temperature for (1) P4VP, (2) S4VP, (3) P2VP, and (4) S2VP, and (b) normalized remanent polarization P_r for (1) P4VP, (2) S4VP, (3) P2VP, and (4) S2VP.

at a temperature lower than the TSC spectrum for P4VP and ends at a temperature higher than the TSC spectrum for P4VP. We wish to point out that the width and peak value of TSC spectrum would depend on the molecular weight and molecular weight distribution of a polymer.

Figure 11b shows the normalized remanent polarization (P_r), defined by eq 1, of P4VP, S4VP diblock copolymer, P2VP, and S2VP diblock copolymer: $P_r = 0.0506$ for P4VP, $P_r = 0.0462$ for S4VP diblock copolymer, $P_r = 0.0366$ for P2VP, and $P_r = 0.0274$ for S2VP diblock copolymer. Notice in Figure 11b that values of P_r were normalized against the poling field because the poling fields were varied for each sample. It can be seen from Figure 11b that $P_r(\text{P4VP}) > P_r(\text{S4VP diblock copolymer}) > P_r(\text{P2VP}) > P_r(\text{S2VP diblock copolymer})$. In view of the fact that remanent polarization of a dielectric material is related to the extent of orientational polarization, we can conclude from Figure 11b that P4VP has a higher orientational polarization than S4VP diblock copolymer, which in turn has a higher orientational polarization than S2VP diblock copolymer, and P2VP has a higher orientational polarization than S2VP diblock copolymer. After all, the lower orientational polarization of S2VP diblock copolymer, as compared with P2VP, is expected because the presence of PS block in the block copolymer has diluted the orientational polarization of P2VP block.

Figure 12 shows plots of dielectric constant (ϵ') vs frequency (ω) at 25 °C for P2VP, P4VP, S2VP diblock copolymer, and S4VP diblock copolymer; namely, the plots compare, over 6 decades of ω , values of ϵ' (a) between P2VP and P4VP, (b) between P4VP and S4VP diblock copolymer, and (c) between S2VP and S4VP diblock copolymers. We already mentioned

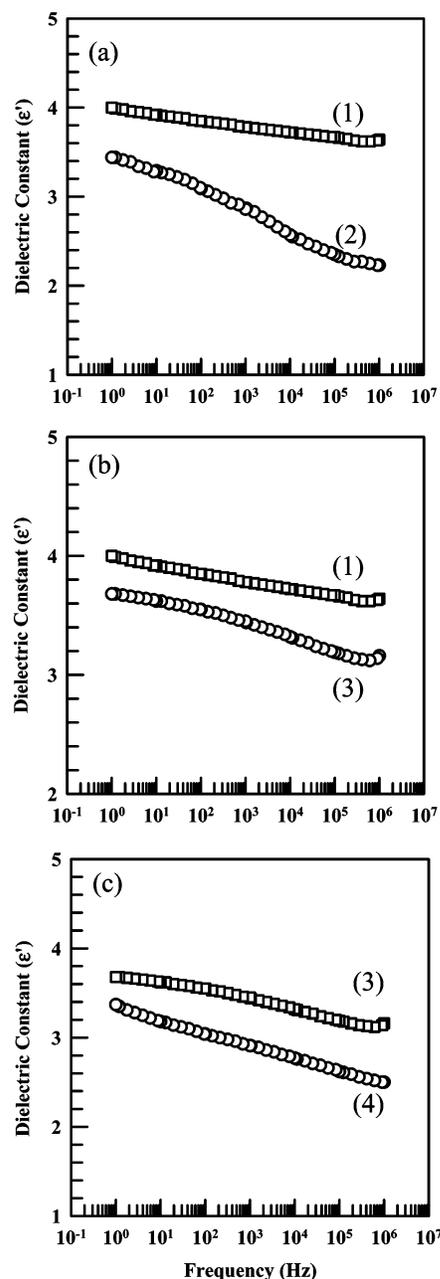


Figure 12. Plots of dielectric constant ϵ' vs angular frequency during the dielectric frequency sweep experiment at 25 °C: (a) comparison between (1) P4VP and (2) P2VP, (b) comparison between (1) P4VP and (3) S4VP, and (c) comparison between (3) S4VP and (4) S2VP.

that the dielectric constant increases with increasing dipole polarization. We can conclude from Figure 12 that (1) the dipole polarization of P4VP is greater than that of P2VP, (2) the dipole polarization of P4VP is greater than that of S4VP diblock copolymer, and (3) the dipole polarization of S4VP diblock copolymer is greater than that of S2VP diblock copolymer. These conclusions are consistent with those made from remanent polarization presented in Figure 11.

In summary, here we have presented evidence that the higher degree of dipole polarization of the P4VP block in S4VP diblock copolymer has led to greater repulsive interactions between the PS and P4VP blocks in an S4VP diblock copolymer, giving rise to large values of “positive” segmental interaction parameter and consequently exceedingly high T_{ODT} of S4VP diblock copolymers, as compared with S2VP diblock copolymers. The experimental observations that $\chi_{PS/P4VP}$ is significantly larger than $\chi_{PS/P2VP}$ at comparable molecular weight and composition

might also be attributable to the fact that the charged nitrogen atom is located farther away from the main chain (C–C bond) in P4VP than in P2VP, increasing the amphiphilicity of P4VP block in S4VP diblock copolymer.³⁷ Therefore, the P4VP block in an S4VP diblock copolymer would be less compatible with the hydrophobic PS block, as compared with the compatibility of the P2VP block in an S2VP diblock copolymer with the hydrophobic PS block.

4. Concluding Remarks

In this study, we synthesized, via sequential anionic polymerization, three nearly monodisperse S2VP diblock copolymers and three nearly monodisperse S4VP diblock copolymers with varying block copolymer compositions and molecular weights. We determined their T_{ODTs} of the block copolymers using oscillatory shear rheometry and SAXS. In this paper, we presented, for the first time, experimental results demonstrating that for comparable molecular weights and block copolymer compositions the T_{ODTs} of S4VP diblock copolymers are exceedingly high as compared with those of S2VP diblock copolymers. To confirm the experimental results, we determined the temperature-dependent segmental interaction parameters for PS/P2VP and PS/P4VP pairs by conducting SAXS experiments with fairly low-molecular-weight S2VP and S4VP diblock copolymers, which were synthesized in our laboratory, in the disordered state. To our knowledge, no investigation has ever been reported on the determination of the temperature-dependent segmental interaction parameters for PS/P2VP and PS/P4VP pairs based on the corresponding block copolymers. The interaction parameters thus determined were tested to predict, via currently held mean-field theory, the T_{ODTs} of the S2VP and S4VP diblock copolymers synthesized in this study. We have found that the predicted T_{ODTs} of the S2VP and S4VP diblock copolymers show the same trend as the experimental results, namely, S4VP diblock copolymers have exceedingly high T_{ODTs} as compared with S2VP diblock copolymers. We conclude that the interaction parameters reported in this paper will be very useful for designing and/or synthesizing vinylpyridine-containing block copolymers in the future.

To explain the origin of the experimentally observed differences in T_{ODT} between S2VP and S4VP diblock copolymers, we conducted TSC and DRS experiments using P2VP, P4VP, S2VP diblock copolymer, and S4VP diblock copolymer. We have found that the dipole polarization of P4VP is greater than that of P2VP, and the dipole polarization of S4VP diblock copolymer is greater than that of S2VP diblock copolymer. We wish to mention that the results of TSC method summarized in this paper has enabled us to make a *qualitative* interpretation of the origin of the difference in ODT between S2VP and S4VP diblock copolymers, which were determined from oscillatory shear rheometry and SAXS. We conclude that the position of the nitrogen atom, whether at 2- or 4- in the pyridine ring, in vinylpyridine block has a profound influence on the T_{ODTs} of the corresponding block copolymers. To our knowledge, such a finding has never been reported in the literature.

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Supporting Information Available: Analysis of SAXS measurements for S2VP-2 specimen and birefringence measurements for S2VP-1 and S2VP-2 specimens. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Hashimoto, T. In *Thermoplastic Elastomer*, 2nd ed.; Holden, G., Legge, N. R., Quirk, R., Schroeder, H. E., Eds.; Hanser: Munich, 1996; Chapter 15A.
- Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
- Han, C. D.; Chun, S. B.; Hahn, S.; Harper, S. Q.; Savickas, P. J.; Meunier, D. M.; Li, L.; Yalcin, T. *Macromolecules* **1998**, *31*, 394.
- Han, C. D.; Choi, S.; Lee, K. M.; Hahn, S. *Macromolecules* **2004**, *37*, 7290.
- Halasa, A. F.; Lohr, D. F.; Hall, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1357.
- Schulz, M. F.; Khandpur, A. K.; Bates, F. S.; Almdal, K.; Mortensen, K.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 2857.
- Leibler, L. *Macromolecules* **1980**, *13*, 1602.
- Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science: New York, 1982; Chapter 4.
- Kokoshko, Z. Yu.; Kitaeva, V. G.; Pushkareva, Z. V.; Blokhin, V. E. *Zh. Obshch. Khim.* **1967**, *37*, 58.
- Lee, D. H.; Kim, H. Y.; Kim, J. K.; Hur, J.; Ryu, D. Y. *Macromolecules* **2006**, *39*, 2027.
- Van Turnhout, J. *Thermally Stimulated Discharge of Polymer Electrets*; Elsevier: Amsterdam, The Netherlands, 1975.
- Teyss edre, G.; Demont, P.; Lacabanne, C. *J. Appl. Phys.* **1996**, *79*, 9258.
- Alegria, A.; Goitiandia, L.; Colmenero, J. *Polymer* **1996**, *37*, 2915.
- Fan, Y.; Wang, X.; Zhang, W.; Lei, Q. *J. Phys. D: Appl. Phys.* **1999**, *32*, 2809.
- Runt, J. P.; Fitzgerald, J. J. Eds. *Dielectric Spectroscopy of Polymeric Materials*; American Chemical Society: Washington, DC, 1977.
- Kaatzte, U.; Giese, K. *J. Phys. E.: Sci. Instrum.* **1980**, *13*, 133.
- Park, C.; Ounaies, Z.; Wise, K. E.; Harrison, J. S. *Polymer* **2004**, *45*, 5417.
- Court, F.; Hashimoto, T. *Macromolecules* **2001**, *34*, 2536.
- (a) Han, C. D.; Kim, J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1741. (b) Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* **1989**, *22*, 383. (c) Han, C. D.; Baek, D. M.; Kim, J. K. *Macromolecules* **1990**, *23*, 561.
- Gouinlock, E. V.; Porter, R. S. *Polym. Eng. Sci.* **1977**, *17*, 535.
- (a) Roe, R.-J.; Fishikis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091. (b) Zin, W.-C.; Roe, R.-J. *Macromolecules* **1984**, *17*, 183.
- Hashimoto, T.; Kowsaka, K.; Shibayama, M.; Kawai, H. *Macromolecules* **1986**, *19*, 754.
- The structure factor $S(q)$ (having the units of cm^3) is related to the coherent contribution of the total scattering intensity by $(\text{d}\Sigma/\text{d}\Omega)_{\text{coh}} = (a_1 - a_2)^2 S(q)$ [Balsara, N. P.; Fetters, L. J.; Hadjichristidis, N.; Lohse, D. J.; Han, C. C.; Graessley, W. W.; Krishnamoorti, R. *Macromolecules* **1992**, *25*, 6137]. Note that the definition of a_i ($i = 1, 2$) (having the units of cm^{-3}) is given by eq 9, and thus $\text{d}\Sigma/\text{d}\Omega$ has the units of cm^{-1} . In this paper, we have introduced a dimensionless structure factor $S'(q)$ by $\text{d}\Sigma/\text{d}\Omega = (V_{\text{ref}}/N_A)(a_1 - a_2)^2 S'(q)$ with V_{ref} being a reference molar volume and N_A being the Avogadro number. However, for convenience, in eq 8 we used the notation S for the dimensionless structure factor.
- It should be mentioned that eqs 13 and 14 must be regarded as being approximate for the reason that S2VP-LMW and S4VP-LWM employed for our SAXS experiments have very low molecular weights (see Table 1) while the Leibler theory,⁷ to which our SAXS data were curve-fitted, is based on an infinite molecular weight of diblock copolymer. There exists a theory due to Fredrickson and Helfand (*J. Chem. Phys.* **1987**, *87*, 607), who considered the finite-size of diblock copolymer chains in the prediction of $(\chi N)_c$, which includes the fluctuation corrections to the Leibler theory. Thus, for a symmetric diblock copolymer ($f = 0.5$) we have $(\chi N)_c = (\chi N)_s + (\chi N)_{\text{fluct}}$ with $(\chi N)_s$ being the spinodal (or mean field) value (10.495) at infinite molecular weight due to the Leibler theory and $(\chi N)_{\text{fluct}}$ being the fluctuation corrections. According to the Fredrickson–Helfand (F–H) theory, $(\chi N)_{\text{fluct}} = 41.022\bar{N}^{-1/3}$ for $f = 0.5$, in which $\bar{N} = N(b^6/v^2)_{\text{PS}}(b^6/v^2)_{\text{P2VP or P4VP}}$ with b being the Kuhn length and v being the molecular volume. However, the F–H theory is only valid for $\bar{N} > 10^4$. It should be pointed out that for the two block copolymers employed in our SAXS experiments we have $\bar{N} = 380$ for S2VP-LMW and $\bar{N} = 100$ for S4VP-LMW, which are much smaller than 10^4 . Under such a circumstance, an application of the F–H theory to the analysis of our SAXS data is not warranted. Inappropriateness of the application of the F–H theory to our SAXS data can be seen from the fact that we obtain $(\chi N)_{\text{fluct}} = 5.7$ for S2VP-LMW and $(\chi N)_{\text{fluct}} = 8.8$ for S4VP-LMW, which are too large to be regarded as being fluctuation corrections. In the past, several research groups erroneously applied the F–H theory to determine a temperature-dependent expression for χ or to estimate the fluctuation-corrected T_{ODT} of very low-molecular-weight ($\bar{N} < 10^3$) diblock copolymers. Such practice should be discouraged in the future.
- Mori, K.; Hasegawa, H.; Hashimoto, T. *Polym. J.* **1985**, *17*, 799.
- Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.
- Russell, T. P.; Hjelm, R. P.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890.
- Dai, K. H.; Kramer, E. J. *Polymer* **1994**, *35*, 157.
- Clarke, C. J.; Eisenberg, A.; La Scala, J.; Rafailovich, M. H.; Sokolov, J.; Li, Z.; Qu, S.; Nguyen, D.; Schwarz, S. A.; Strzhemechny, Y.; Sauer, B. B. *Macromolecules* **1997**, *30*, 4184.
- Alberda van Ekenstein, G. O. R.; Mayboom, R.; ten Brinke, G.; Ikkala, O. *Macromolecules* **2000**, *33*, 3752.
- Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5096.
- Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5112.
- Freed, K. F.; Dudowicz, J. *J. Chem. Phys.* **1992**, *97*, 2105.
- Dudowicz, J.; Freed, K. F. *Macromolecules* **1993**, *26*, 213.
- Agnew, N. H. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2819.
- Kuo, S.-W.; Lin, C.-L.; Chang, F.-C. *Polymer* **2002**, *43*, 3943.
- Vasilevskaya, V. V.; Khalatur, P.; Khokhlov, A. R. *Macromolecules* **2003**, *36*, 10103.

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