Effect of the Microstructure of Polydiene Block on Order−Disorder Transition in Diblock Copolymers Containing Polystyrene Block or Poly(vinylcyclohexane) Block

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ABSTRACT: The effect of the microstructure of polydiene blocks on order−disorder transition (ODT) in diblock copolymers containing polystyrene (PS) or poly(vinylcyclohexane) (PVCH) blocks was investigated. For the study, a series of polystyrene-*block*-polybutadiene (SB diblock) copolymers with varying microstructures in the polybutadiene (PB) block and polystyrene-*block*-polyisoprene (SI diblock) copolymers with varying microstructures in the polyisoprene (PI) block were synthesized. Subsequently, either only the PB block in an SB diblock copolymer was selectively saturated to obtain PS-*block*-poly(ethylene-*co*-1-butene) (PEB) copolymer or both blocks were saturated to obtain PVCH-*block*-PEB copolymer. Also, either only the PI block in an SI diblock copolymer was selectively saturated to obtain PS-*block*-poly(ethylene-*alt*-propylene) (PEP) copolymer or both blocks were saturated to obtain PVCH-*block*-PEP copolymer. The ODT temperature (T_{ODT}) of each block copolymer was determined from oscillatory shear rheometry. It has been found that (i) the T_{ODT} of an SB diblock copolymer with predominantly 1,2-addition in the PB block is much higher than that of an SB diblock copolymer with predominantly 1,4-addition in the PB block, (ii) the T_{ODT} of an SI diblock copolymer with high vinyl content (predominantly 3,4- and 1,2-additions) in the PI block is much higher than that of an SI diblock copolymer with predominantly 1,4-addition in the PI block, (iii) the T_{ODT}s of PS-*block*-PEB and PS-*block*-PEP copolymers are considerably higher (>100 °C) than those of the unsaturated precursors regardless of the microstructures of polydiene block, and (iv) the T_{ODT}s of PVCH-*block*-PEB and PVCH-*block*-PEP copolymers are higher or lower than those of the unsaturated precursors depending upon the microstructure of polydiene block. By curve fitting the experimental phase diagrams, which were obtained from cloud point measurement, to the theoretical phase diagrams based on the Flory−Huggins theory, temperature-dependent segment−segment interaction parameters (χ) were determined for PS/PB, PS/PEB, PVCH/PEB, PS/PI, PS/PEP, and PVCH/PEB pairs with varying microstructures of polydienes. It is found that while values of χ for the polymer pairs thus determined explain satisfactorily the experimentally determined T_{ODT}s of all the block copolymers investigated, the conformational asymmetry parameter (ϵ) explains the experimentally determined T_{ODT}s of the completely saturated PVCH-*block*-PEB and PVCH-*block*-PEP copolymers, but not of the partially saturated PS-*block*-PEB and PS-*block*-PEP copolymers. Further, it is found that values of ϵ do not explain the effect of microstructures of PB block on the T_{ODT} of SB diblock copolymer with varying microstructures. Thus, we conclude that a correlation between ϵ and χ seems to exist for completely saturated block copolymers, but not for partially saturated block copolymers.

1. Introduction

It has been reported that the microstructure of polybutadiene (PB) block in a polystyrene-*block*-polybutadiene (SB diblock) copolymer or polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS triblock) copolymer influences greatly the mechanical properties (e.g., rolling resistance and traction) of automobile tires.[1] This can be easily understood from the point of view that PBs with different microstructures have vastly different glass transition temperatures (T_g) and/or melting temperatures (T_m), moduli, melt viscosities, and entanglement molecular weights.[2] It is then clear that different proportions of 1,2- and 1,4-additions in the PB block of an SB diblock or SBS triblock copolymer can give rise to vastly different physical and mechanical properties.

It has also been reported that the microstructure of PB, when blended with polystyrene (PS), for instance, has a profound influence on the phase behavior of the blend[3] because the segment−segment interactions between PS and PB are greatly affected by the microstructure of PB. This observation can be extended to the phase behavior of SB diblock copolymer. For example, the order−disorder transition (ODT) temperature (T_{ODT}) of SB diblock copolymer will vary with the microstructure of the PB block because the microstructure of PB block affects segment−segment interactions between PS and PB phases. The same observation can be made to polystyrene-*block*-polyisoprene (SI diblock) copolymers or polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS triblock) copolymers with varying microstructures (1,2-, 3,4-, and 1,4-additions) of polyisoprene (PI) block.

It is well established that the T_{ODT} of a block copolymer depends on the extent of segment−segment interactions of the constituent components, degree of polymerization, and block composition.[4,5] During the past two decades, numerous papers have been published on ODT in block copolymers, and this work has been extensively reviewed.[6,7] However, relatively little has been reported on the effect of the microstructures of polydiene block on the ODT in SB, SBS, SI, or SIS block copolymers.

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Table 1. Summary of the Molecular Characteristics of the Diblock Copolymers Investigated in This Study

sample code	M_n	M_w/M_n[a]	wt frac of PS or PVCH	microstructure of PB or PI block
$SB^{1,4}$-14/11	2.40×10^4 [b]	1.06	0.54	91% 1,4-addition
PS−$PEB^{1,4}$-14/11	2.44×10^4 [c]	1.07	0.53	
PVCH−$PEB^{1,4}$-14/11	2.51×10^4 [c]	1.07	0.54	
$SB^{1,4}$-12/12	2.38×10^4 [b]	1.05	0.50	93% 1,4-addition
$SB^{1,2}$-7/16	2.30×10^4 [b]	1.02	0.31	91% 1,2-addition
PS−$PEB^{1,2}$-7/16	2.36×10^4 [c]	1.03	0.30	
PVCH−$PEB^{1,2}$-7/16	2.40×10^4 [c]	1.03	0.31	
$SB^{1,2}$-11/11	2.25×10^4 [b]	1.07	0.50	86% 1,2-addition
$SI^{1,4}$-10/9	1.88×10^4 [b]	1.09	0.54	94% 1,4-addition
PS−$PEP^{1,4}$-10/9	1.90×10^4 [c]	1.10	0.53	
PVCH−$PEP^{1,4}$-10/9	1.96×10^4 [c]	1.10	0.55	
$SI^{3,4}$-10/10	2.00×10^4 [b]	1.05	0.53	high vinyl content[d]
PS−$PEP^{3,4}$-10/10	2.03×10^4 [c]	1.06	0.54	
PVCH−$PEP^{3,4}$-10/10	2.10×10^4 [c]	1.06	0.54	

[a] Determined from GPC. [b] Determined from membrane osmometry. [c] Calculated from stoichiometry. [d] 59% 3,4-addition and 34% 1,2-addition.

In the past, ODT in poly(vinylcyclohexane) (PVCH)-*block*-poly(ethylene-*co*-1-butene) (PEB) copolymer that was obtained from complete saturation of an SB diblock copolymer and in PVCH-*block*-poly(ethylene-*alt*-propylene) (PEP) copolymer that was obtained from complete saturation of an SI diblock copolymer has been investigated. Some investigators[8−11] reported that the T_{ODT}s of PVCH-*block*-PEB and PVCH-*block*-PEP copolymers were higher than the unsaturated precursors with predominantly 1,4-addition in the polydiene blocks, while others[9] reported that the T_{ODT}s of PVCH-*block*-PEB copolymers were lower than the unsaturated precursors with predominantly 1,2-addition in the PB block. While the calculations of the interaction parameters (χ) for PVCH/PEB and PVCH/PEP pairs from group contribution methods could not explain the experimental results, Gehlsen and Bates[8,9] explained the experimentally observed increase or decrease in T_{ODT} of PVCH-*block*-PEB or PVCH-*block*-PEP copolymers in terms of a change in conformational asymmetry parameter (ϵ) between different species after saturation of an SB or SI diblock copolymer.

However, no study has been reported on whether the T_{ODT} of PVCH-*block*-PEP copolymer can be lower than the unsaturated precursor with predominantly vinyl content (3,4- and 1,2-additions) in the PI block. Only one study[11] has been reported on the T_{ODT} of partially saturated PS-*block*-PEP copolymer, showing that its T_{ODT} is exceedingly high compared to that of the unsaturated precursor with predominantly 1,4-addition in the PI block. However, no study has been reported on whether the same trend may hold for partially saturated PS-*block*-PEB copolymer obtained from an SB diblock copolymer with predominantly 1,4-addition in the PB block and whether the T_{ODT} of partially saturated PS-*block*-PEP copolymers may be higher or lower than the unsaturated precursor with predominantly vinyl content (3,4- and 1,2-additions) in the PI block.

The purpose of this paper is to first present the experimental results of our recent investigation on the effect of microstructures of unsaturated or saturated polydiene block on the T_{ODT} of diblock copolymers containing PS or PVCH block and then offer an interpretation of the experimental results using the χ parameter. For the study, we synthesized a series of SB and SI diblock copolymers with varying microstructures (predominantly 1,4-addition or predominantly vinyl content) and prepared not only partially saturated PS-*block*-PEB and PS-*block*-PEP copolymers but also completely saturated PVCH-*block*-PEB and PVCH-*block*-PEP copolymers to investigate ODT. We interpret the experimentally determined T_{ODT} using the temperature-dependent χ parameter for PS/PB, PS/PEB, PVCH/PEB, PS/PI, PS/PEP, and PVCH/PEB pairs with varying microstructures of polydienes. Expressions for temperature-dependent χ were obtained by curve fitting the experimental phase diagram, which was obtained from cloud point measurements,[12] to the theoretical phase diagram based on the Flory−Huggins theory. In this paper, we show that an increasing or decreasing trend of predicted T_{ODT}s, via the Leibler theory,[4] of the PS-*block*-PEB, PS-*block*-PEP, PVCH-*block*-PEB, and PVCH-*block*-PEP copolymers is in agreement with experimental results. Further, we show that a change in ϵ between two different species after complete saturation of an SB or SI diblock copolymer explains the experimental observation of the increase or decrease in the T_{ODT} of completely saturated PVCH-*block*-PEB and PVCH-*block*-PEP copolymers, but ϵ cannot explain the dramatic increase in the T_{ODT} of partially saturated PS-*block*-PEB and PS-*block*-PEP copolymers and the effect of microstructures of PB block on the T_{ODT} of SB diblock copolymer observed experimentally.

2. Experimental Section

2.1. Materials and Characterization. We synthesized, via sequential anionic polymerization, four SB diblock copolymers and two SI diblock copolymers with varying microstructures of polydiene block. Using well-established standard procedures, SI diblock copolymers with predominantly high 1,4-addition in the PI block were synthesized in cyclohexane as solvent, while SI diblock copolymers with high vinyl content (predominantly 3,4- and 1,2-additions) in the PI block were synthesized in tetrahydrofuran (THF) as solvent. In both cases *sec*-butyllithium was used as initiator. The details of the procedures employed for the synthesis of SB diblock copolymers with varying microstructures of PB block are described in our previous papers.[3] Table 1 gives a summary of the molecular characteristics of the SB and SI diblock copolymers synthesized in this study. The number-average molecular weight (M_n) was determined using membrane osmometry (Jupiter Instrument), and the polydispersity index was determined using a gel permeation chromatograph (GPC) (Waters). The microstructures of polydiene block in an SB or SI diblock copolymer and the weight fraction of PS in an SB or SI diblock copolymer were determined using ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and the results are summarized in Table 1. For convenience, below we will use the following notations: $PI^{1,4}$ and $PB^{1,4}$ describing the polydienes with predominantly 1,4-addition; $PI^{3,4}$ and $PB^{1,2}$ describing the polydienes with predominantly 3,4-addition and 1,2-addition, respectively; $PEP^{1,4}$ and $PEB^{1,4}$ describing the saturated polymers obtained from the unsaturated precursors $PI^{1,4}$ and $PB^{1,4}$, respectively; $PEP^{3,4}$ and $PEB^{1,2}$ describing the saturated polymers obtained from the unsaturated precursors $PI^{3,4}$ and $PB^{1,2}$, respectively.

Portions of the SB and SI diblock copolymers synthesized were partially saturated (only the polydiene block was hydrogenated) to obtain PS-*block*-PEB and PS-*block*-PEP copolymers, and the remainder was completely saturated to obtain PVCH-*block*-PEB and PVCH-*block*-PEP copolymers.

An SB diblock copolymer was partially saturated to obtain PS-*block*-PEB copolymer, using a 500 mL glass reactor (Parr Instrument, model 3921) at a moderate pressure of 0.423 MPa (50 psig). The experimental procedures employed are as follows. A 0.0306 M solution of catalyst was prepared by slowly adding 5.38 g of a cobalt(II) 2-ethylhexanoate solution (Aldrich, 65 wt % solution in mineral spirit) over a period of 30 min to a solution of 35 mL of triethylaluminum (Aldrich, 1.0 M solution in hexane) in 300 mL of purified cyclohexane. A mixture of aluminum cobalt with a molar ratio of 3.45 was used to selectively hydrogenate 1,2- or 1,4-addition in the PB block of an SB diblock copolymer. Next, 2 g of SB diblock copolymer was dissolved in 200 mL of purified cyclohexane in a 500 mL flask under vacuum. After the SB diblock copolymer was dissolved in cyclohexane, the flask was charged with argon gas, and then the solution was transferred to a 500 mL reactor with a septum. The reactor was evacuated twice and then charged with hydrogen (Praxair, 99.9999%). Under positive hydrogen pressure, 0.3 mol % (based on butadiene units) of a cobalt(II) 2-ethylhexanoate triethylaluminum catalyst solution was added to the reactor with a gastight syringe through a septum port. The reactor was then sealed and heated to 55 °C. Hydrogen was supplied to the reactor at 0.423 MPa (50 psig), while stirring throughout the entire period of hydrogenation. After a reaction time of 1 h, the polymer solution was washed with dilute aqueous acetic acid to remove residual catalyst, and the polymer was precipitated using an excess amount of methanol. The precipitated polymer was filtered and dried for 3 days at room temperature first in a fume hood and then at 60 °C in a vacuum oven.

An SI diblock copolymer was partially saturated to obtain PS-*block*-PEP copolymer using a 2 L pressure reactor (Parr Instrument Co.) equipped with a gas dispersion impeller at 1.93 MPa (280 psig) hydrogen pressure. A solution of 2.17 g of $SI^{1,4}$-10/9 in 600 mL of cyclohexane (HPLC grade, Fisher Chemical) was prepared by dissolving the polymer in a 1 L round-bottom flask and transferring the solution to the reactor by addition funnel. The reactor headspace was then purged three times with nitrogen (BOC, 99.999%). A 0.077 M solution of catalyst was prepared by adding 20 mL of a 0.1 M nickel(II) 2-ethylhexanoate solution (prepared by dilution of a 10% nickel solution in mineral spirits obtained from Shepherd Chemical) to a dry, nitrogen-filled flask on a vacuum line. The flask was cooled with an ice bath, and 6 mL of a 1 M triethylaluminum solution in heptane (Aldrich Chemical) was added dropwise to the flask, forming a black suspension. This solution was stirred for 20 min and then transferred by syringe to the reactor. The reactor was purged twice with nitrogen and then charged with hydrogen (BOC, 99.9995%). The reactor was sealed, and the contents were stirred and heated to 70 °C for 12 h. The hydrogen was vented, and the cooled solution was removed from the reactor. The polymer solution was stirred over a 10% aqueous citric acid solution for 48 h, the polymer solution was filtered, and the polymer was isolated by precipitation from methanol and was dried in a vacuum oven at 60 °C for 2 h. 2.0 g of polymer was isolated.

Complete saturation of an SB or SI diblock copolymer to obtain PVCH-*block*-PEB or PVCH-*block*-PEP copolymers required much higher pressure at 8.96 MPa (1300 psig). Below, for illustration we describe the experimental procedures employed[13] to hydrogenate an SB diblock copolymer ($SB^{1,2}$-7/16) to obtain a PVCH-*block*-PEB copolymer (PVCH−$PEB^{1,2}$-7/16). First, 5 g of $SB^{1,2}$-7/16 having 91% 1,2-addition in PB block was dissolved in 800 mL of cyclohexane and was added to the 2 L Parr reactor. A slurry containing 5 g of Pt/SiO_2 catalyst[14] in 200 mL of cyclohexane was prepared in a stainless steel cylinder equipped with air-free quick disconnecting fittings, and the slurry was transferred to the reactor with a slight overpressure of nitrogen. The reactor was purged twice with hydrogen, and the hydrogen pressure was set at 8.96 MPa (1300 psig). The reactor was then sealed and heated to 170 °C with stirring, and the reaction was allowed to proceed for 3 h. After this time the reactor was allowed to cool to room temperature and the excess hydrogen was vented. The polymer solution was separated from the catalyst using a 0.2 μm PFTE membrane filter, and the polymer was isolated by precipitation from methanol. After drying in a vacuum oven to remove residual solvent, the isolated polymer weighed 2.5 g. ^{1}H NMR analysis showed no detectable resonances due to the polybutadiene alkenes or the polystyrene phenyl rings present in the starting material, but only a sharp resonance due to the ethyl side chain methyl group protons at 0.80 ppm and a broad resonance ranging from 0.8 to 1.8 ppm. Similar procedures were used to hydrogenate other SB diblock copolymers and two SI diblock copolymers ($SI^{1,4}$-10/9 and $SI^{3,4}$-10/10) synthesized in this study (see Table 1).

2.2. Sample Preparation. Samples for oscillatory shear rheometry were prepared by first dissolving a predetermined amount of a block copolymer (10 wt % in solution) in the presence of 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in a fume hood slowly at room temperature for 1 week, and the last trace of solvent was removed by drying the samples in a vacuum oven at an elevated temperature for varying periods, depending upon the block copolymer. The drying of the samples was continued until there was no further change in weight, and then the specimens were stored in a refrigerator.

2.3. Oscillatory Shear Rheometry. An Advanced Rheometric Expansion System (ARES, Rheometric Scientific) was used in the oscillatory mode with parallel plate fixtures (25 mm diameter). Dynamic frequency sweep experiments were conducted; i.e., the dynamic storage modulus (G') and dynamic loss modulus (G'') were measured as functions of angular frequency (ω) ranging from 0.01 to 100 rad/s at various temperatures. The temperature increment in the frequency sweep experiment varied from 3 to 10 °C, and the specimen was kept at a constant temperature for 30−40 min before rheological measurements actually began. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ±1 °C. For the rheological measurements, the strain was varied from 0.03 to 0.3 depending upon the measurement temperature, which was well within the linear viscoelastic range for the materials investigated. Dynamic temperature sweep experiments under isochronal conditions were also conducted; i.e., G' was measured at $\omega = 0.1$ rad/s during heating. All experiments were conducted under a nitrogen atmosphere to preclude oxidative degradation of the samples.

3. Results and Discussion

3.1. Experimental Determination of the T_{ODT}s of Completely Saturated PVCH-*block*-PEB and PVCH-*block*-PEP Copolymers, Partially Saturated PS-*block*-PEB and PS-*block*-PEP Copolymers, and Unsaturated Precursors. Figure 1a gives log G' vs log G'' plots for $SB^{1,4}$-14/11 at various temperatures. It is seen in Figure 1a that the log G' vs log G'' plots have a slope of 2 in the terminal region and begin to be independent of temperature at ca. 175 °C. Following the rheological criterion of Han and co-workers,[15] we determine the T_{ODT} of $SB^{1,4}$-14/11 to be ca. 175 °C. The inset of Figure 1a describes the results of the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s, showing that G' begins to drop precipitously at ca. 173 °C. Following the rheological criterion of Gouinlock and Porter,[16] we determine the T_{ODT} of $SB^{1,4}$-14/11 to be ca. 173 °C, which is in good agreement with that determined from the log G' vs log G'' plots. Figure 1b

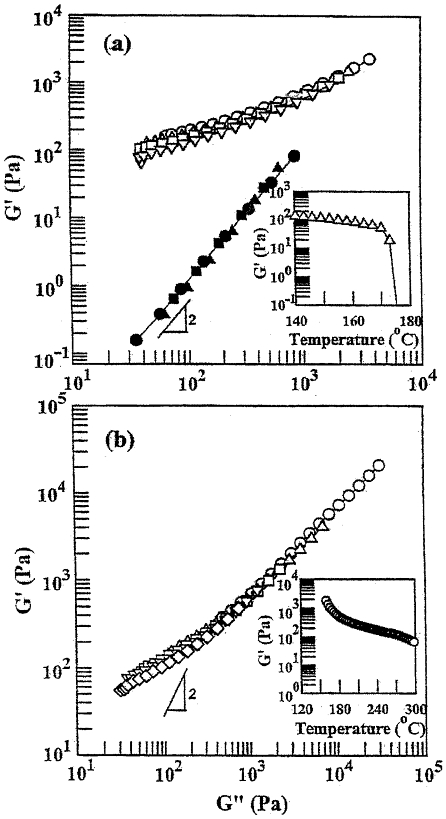

Figure 1. (a) Plots of log G' vs log G'' for SB^{1,4}-14/11 at various temperatures: (○) 150, (△) 160, (□) 165, (▽) 170, (●) 175, (▲) 180, and (■) 185 °C. The inset gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s. (b) Plots of log G' vs log G'' for PVCH−PEB^{1,4}-14/11 at various temperatures: (○) 170, (△) 200, (□) 240, (▽) 270, and (◇) 300 °C. The inset gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s.

gives log G' vs log G'' plots for PVCH−PEB^{1,4}-14/11 at various temperatures. In Figure 1b, we observe that log G' vs log G'' plots exhibit a slope much *less* than 2 in the terminal region over the entire range of temperatures tested up to 300 °C, the highest experimental temperature employed. From the log G' vs log G'' plots we conclude that microdomain structure of PVCH−PEB^{1,4}-14/11 still persists even at 300 °C, indicating that the block copolymer has $T_{\rm ODT}$ much higher than the unsaturated precursor SB^{1,4}-14/11. This conclusion is supported by the results of the isochronal dynamic temperature sweep experiment, given in the inset of Figure 1b, because values of G' remain high even at 300 °C without showing any indication that G' begins to drop precipitously. Comparison of Figure 1b with Figure 1a indicates that the $T_{\rm ODT}$ of PVCH−PEB^{1,4}-14/11 is more than 125 °C higher than that of the unsaturated precursor, SB^{1,4}-14/11. Earlier, similar results were reported by Gehlsen and Bates,[9] who reported that after complete saturation the $T_{\rm ODT}$ of an SB^{1,4} diblock copolymer (1,4-PB−PS-1) increased from 98 to 235 °C, and also by Adams et al.,[10] who reported that after complete saturation the $T_{\rm ODT}$ of an SB^{1,4} diblock copolymer (S/B-62) increased from 107 ± 3 to 231 ± 3 °C.

A large increase in $T_{\rm ODT}$, upon complete saturation of SB^{1,4}-14/11, observed in Figure 1 suggests that the segment−segment interaction between the PVCH and PEB^{1,4} blocks in PVCH−PEB^{1,4}-14/11 became strongly repulsive (i.e., the miscibility between the PVCH and PEB^{1,4} decreased considerably) compared to that between the PS and PB^{1,4} blocks in SB^{1,4}-14/11. In a previous paper[12] we have shown that the segment−segment interaction between PVCH and PEB^{1,4} in binary blends is much more repulsive than that between PS and PB^{1,4} in binary blends. Therefore, we conclude that the very large increase in $T_{\rm ODT}$, observed in the previous studies[9,10] and also in the present study, upon complete saturation of an SB^{1,4} diblock copolymer has originated from an increase in the *repulsive* segment−segment interactions between PVCH and PEB.^{1,4}

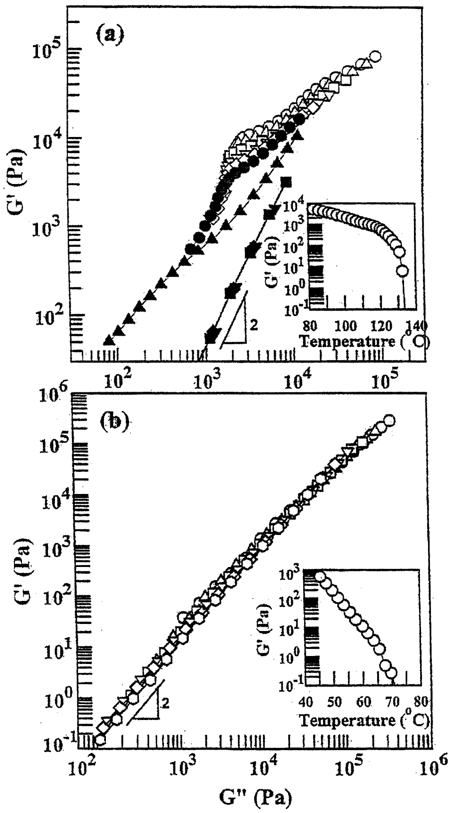

Figure 2. (a) Plots of log G' vs log G'' for SB^{1,2}-7/16 at various temperatures: (○) 80, (△) 90, (□) 100, (▽) 110, (◇) 120, (●) 130, (▲) 133, (■) 136, (▼) 140, and (◆) 145 °C. The inset gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s. (b) Plots of log G' vs log G'' for PVCH−PEB^{1,2}-7/16 at various temperatures: (○) 50, (△) 55, (□) 60, (▽) 65, (◇) 70, and (⬡) 75 °C. The inset gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s.

Figure 2a gives log G' vs log G'' plots for SB^{1,2}-7/16 at various temperatures, which were obtained during heating. It is seen in Figure 2a that log G' vs log G'' plots with a slope of 2 in the terminal region begin to exhibit temperature independence at 136 °C, from which we conclude that the $T_{\rm ODT}$ of SB^{1,2}-7/16 is ca. 136 °C. The inset of Figure 2a gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s, showing a precipitous drop of G' at ca. 132 °C, which is very close to the $T_{\rm ODT}$ determined from the log G' vs log G'' plots.

Figure 2b gives log G' vs log G'' plots for PVCH−PEB^{1,2}-7/16 at various temperatures, exhibiting a slope of 2 in the terminal region and temperature independence over the entire range of temperatures tested, usually observed in linear flexible homopolymers.[17] This observation leads us to conclude that PVCH−PEB^{1,2}-7/16 is in the disordered state over the entire range of temperatures tested. This conclusion is supported by the results of the isochronal dynamic temperature sweep experiment given in the inset of Figure 2b in that G' steadily decreases with increasing temperature, again behavior usually observed in linear flexible homopolymers. That is, the cylinder-forming diblock copolymer $SB^{1,2}$-7/16 having $T_{ODT} \approx 136$ °C has transformed, after complete saturation, into a disordered diblock copolymer $PVCH-PEB^{1,2}$-7/16. This observation indicates that the T_{ODT} of an $SB^{1,2}$ diblock copolymer, after saturation, becomes lower than that of the unsaturated precursor when the microstructure of the PB block has predominantly 1,2-addition. Earlier, Gehlsen and Bates[9] reported similar observations.

It is very clear from Figures 1 and 2 that the microstructure of the PB block in an SB diblock copolymer has a pronounced influence on the T_{ODT} of completely saturated PVCH-*block*-PEB copolymer. What is of great interest here is that after complete saturation of an SB diblock copolymer the T_{ODT} of PVCH-*block*-PEB copolymer can be higher or lower than that of the unsaturated precursor, depending upon the microstructures of PB block. In our previous paper[12] we have shown that the segment–segment interaction between PVCH and $PEB^{1,2}$ in $PVCH/PEB^{1,2}$ blends becomes less repulsive (i.e., the miscibility of PVCH and $PEB^{1,2}$ increases) as the 1-butene content in the $PEB^{1,2}$ increases.

On the basis of cloud point measurements, in our previous paper[12] we reported that the miscibility of PS/PB pairs having a PB with predominantly 1,2- or 1,4-addition and the saturated counterparts increases in the order $PS/PB^{1,2} < PVCH/PEB^{1,4} < PS/PB^{1,4} < PVCH/PEB^{1,2}$. The above relationship can be expressed by the following inequalities

$$\chi_{PS/PB^{1,2}} > \chi_{PVCH/PEB^{1,4}} > \chi_{PS/PB^{1,4}} > \chi_{PVCH/PEB^{1,2}}$$

in terms of the Flory–Huggins interaction parameter χ, describing the effect of the microstructures of PB on the segment–segment interactions of PS/PB and PVCH/PEB binary blends. Such inequalities now explain why the T_{ODT} of PVCH-*block*-PEB copolymer may increase (see Figure 1) or decrease (see Figure 2), depending upon the microstructures of polydiene block, after an SB diblock copolymer is completely saturated.

To compare the melt viscosities of $SB^{1,2}$-7/16 before and after complete saturation, in Figure 3 we have prepared log $|\eta^*|$ vs log ω plots for $SB^{1,2}$-7/16 and $PVCH-PEB^{1,2}$-7/16, where $|\eta^*|$ is complex viscosity defined by $|\eta^*| = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$. In Figure 3b we observe that $PVCH-PEB^{1,2}$-7/16 exhibits Newtonian behavior over the entire range of temperatures tested, whereas in Figure 3a we observe that $SB^{1,2}$-7/16 shows shear-thinning behavior over the entire range of ω tested at temperatures *below* 136 °C (which is the T_{ODT} of $SB^{1,2}$-7/16) and then Newtonian behavior at 136 °C and higher temperatures. Notice in Figure 3a that at $\omega = 0.01$ rad/s the $|\eta^*|$ at 130 °C is about 3 orders of magnitude greater than that at 136 °C. Such a large difference in $|\eta^*|$ at temperatures between 130 and 136 °C signifies that at 136 °C $SB^{1,2}$-7/16 has lost long-range order transforming into a disordered phase. It is well-established today that the shear-thinning behavior of a microphase-separated block copolymer at very low values of ω is due to the presence of microdomains. It is interesting to observe in Figure 3b that oscillatory shear measurements of $PVCH-PEB^{1,2}$-7/16 were conducted at a temperature as low as 50 °C, although the glass transition temperature (T_g) of neat PVCH having a molecular weight of 7000 is ca. 95 °C. Unless there was very good miscibility between PVCH and $PEB^{1,2}$ blocks in $PVCH-PEB^{1,2}$-7/16 such that the T_g of PVCH was decreased to below 50 °C, the oscillatory shear measurements at 50 °C would not have been possible. This observation now explains why in Figure 2b we could not determine the T_{ODT} of $PVCH-PEB^{1,2}$-7/16.

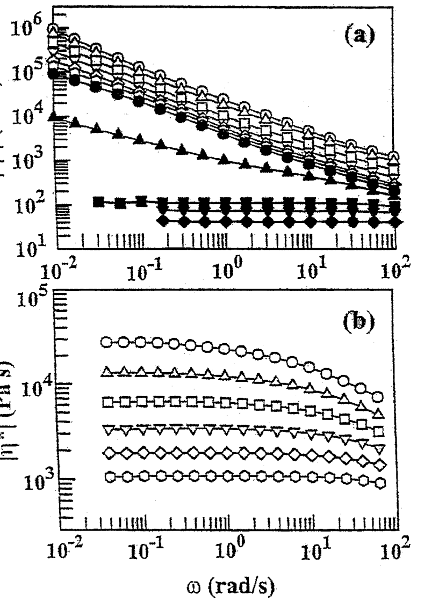

Figure 3. (a) Plots of log $|\eta^*|$ vs log ω for $SB^{1,2}$-7/16 at various temperatures: (○) 80, (△) 90, (□) 100, (▽) 110, (◇) 120, (●) 130, (▲) 133, (■) 136, (▼) 140, and (◆) 145 °C. (b) Plots of log $|\eta^*|$ vs log ω for $PVCH-PEB^{1,2}$-7/16 at various temperatures: (○) 50, (△) 55, (□) 60, (▽) 65, (◇) 70, and (⬡) 75 °C.

Using the same experimental methods described above, we investigated ODT in PVCH-*block*-PEP copolymers upon complete saturation of two SI diblock copolymers: $SI^{1,4}$-10/9 and $SI^{3,4}$-10/10, namely, we determined the T_{ODT} of $PVCH-PEP^{1,4}$-10/9 to be ca. 169 °C, which is ca. 13 °C higher than that of the unsaturated precursor $SI^{1,4}$-10/9 with predominantly 1,4-addition (see Table 2). In our previous paper[12] we have shown that the segment–segment interaction between PVCH and $PEP^{1,4}$ in $PVCH/PEP^{1,4}$ blends becomes more *repulsive* (i.e., the miscibility of PVCH and $PEP^{1,4}$ decreases) than that between PS and $PI^{1,4}$ in $PS/PI^{1,4}$ blends. Such phase behavior of $PVCH/PEP^{1,4}$ blends now explains why the T_{ODT} of $PVCH-PEP^{1,4}$-10/9 is higher than that of $SI^{1,4}$-10/9.

On the other hand, we found that upon complete saturation $SI^{3,4}$-10/10 with very high vinyl content (59% 3,4-addition and 34% 1,2-addition) in the PI block has transformed into a disordered block copolymer $PVCH-PEP^{3,4}$-10/10, while the T_{ODT} of $SI^{3,4}$-10/10 is ca. 140 °C (see Table 2).

We attribute a decrease in T_{ODT} of $PVCH-PEP^{3,4}$-10/10, upon complete saturation of $SI^{3,4}$-10/10, to an increased miscibility between PVCH and $PEP^{3,4}$ blocks. In our previous paper[12] we have shown that the segment–segment interaction between PVCH and $PEP^{3,4}$ in $PVCH/PEP^{3,4}$ blends becomes *less repulsive* (i.e., the miscibility of PVCH and $PEP^{3,4}$ increases) than that between PS and $PI^{3,4}$ in $PS/PI^{3,4}$ blends.

On the basis of cloud point measurements, in our previous paper[12] we reported that the miscibility of PS/PI pairs having a PI with high vinyl content and the saturated counterparts increases in the order $PS/PI^{3,4}$

Table 2. Summary of Measured and Predicted T_{ODT}s, ϵ, and α for the Block Copolymers Investigated in This Study

sample code	measured T_{ODT} (°C)	predicted T_{ODT} (°C)	ϵ (150 °C)	$\alpha \times 10^3$ (150 °C)
(a) with predominantly 1,4-addition in PB block				
$SB^{1,4}$-14/11	175	135[a]	1.58	0.329[a]
PS−$PEB^{1,4}$-14/11	>300	**360**[b]	2.08	**1.324**[b]
PVCH−$PEB^{1,4}$-14/11	>300	162[c]	2.28	0.460[c]
(b) with predominantly 1,2-addition in PB block				
$SB^{1,2}$-7/16	136	141[d]	1.26	0.567[d]
PS−$PEB^{1,2}$-7/16	250	**298**[e]	1.21	**1.106**[e]
PVCH−$PEB^{1,2}$-7/16	*n*	97[f]	1.10	0.176[f]
(c) with predominantly 1,4-addition in PI block				
$SI^{1,4}$-10/9	156	107[g]	1.22	0.275[g]
PS−$PEP^{1,4}$-10/9	>300	**128**[h]	1.33	**0.426**[h]
PVCH−$PEP^{1,4}$-10/9	169	114[i]	1.45	0.332[i]
(d) with predominantly vinyl content (3,4- and 1,2-additions) in PI block				
$SI^{3,4}$-10/10	140	200[j]	1.22	0.897[j]
PS−$PEP^{3,4}$-10/10	>300	**225**[k]	NA	**1.122**[k]
PVCH−$PEP^{3,4}$-10/10	*n*	91[m]	NA	0.253[m]

[a] Using eq 8. [b] Using eq 9. [c] Using eq 10. [d] Using eq 12. [e] Using eq 13. [f] Using eq 14. The T_{ODT} lies below the T_g (120 °C) of PVCH-10. [g] Using eq 2. [h] Using eq 3. [i] Using eq 4. [j] Using eq 5. [k] Using eq 6. [m] Using eq 7. The T_{ODT} lies below the T_g (120 °C) of PVCH-10. NA denotes "not available". [n] Disordered.

< PVCH/$PEP^{1,4}$ < PS/$PI^{1,4}$ < PVCH/PEP.^{3,4} The above relationship can be expressed by the following inequalities

$$\chi_{PS/PI^{3,4}} > \chi_{PVCH/PEP^{1,4}} > \chi_{PS/PI^{1,4}} > \chi_{PVCH/PEP^{3,4}}$$

in terms of χ, describing the effect of the microstructures of PI on the segment−segment interactions of PS/PI and PVCH/PEP binary blends. Such inequalities now explain why the T_{ODT} of PVCH-*block*-PEP copolymer may increase or decrease (see Table 2), depending upon the microstructure of the polydiene block, upon complete saturation of an SI diblock copolymer.

Using the experimental methods described above, we have determined the T_{ODT}s of partially saturated diblock copolymers: PS−$PEB^{1,4}$-14/11, PS−$PEB^{1,2}$-7/16, PS−$PEP^{1,4}$-10/9, and PS−$PEP^{3,4}$-10/10, the results of which are summarized in Table 2. It is interesting to observe in Table 2 that the values of T_{ODT}s of partially saturated diblock copolymers are much higher than those of completely saturated diblock copolymers and unsaturated precursors. This observation is in general agreement with that reported previously by Lai et al.[11]

The T_{ODT} measurements for partially saturated PS-*block*-PEP and PS-*block*-PEB copolymers, and completely saturated PVCH-*block*-PEP and PVCH-*block*-PEB copolymers, summarized in Table 2 are supported by the phase behavior of binary blends that consist of (i) PS and $PI^{1,4}$, (ii) PS and $PEP^{1,4}$, (iii) PVCH and $PEP^{1,4}$, (iv) PS and $PB^{1,4}$, (v) PS and $PEB^{1,4}$, or (vi) PVCH and $PEB^{1,4}$. Figure 4a gives phase diagrams for (PS-6)/($PI^{1,4}$-5), (PS-6)/($PEP^{1,4}$-5), and (PVCH-6)/($PEP^{1,4}$-5) blends, and Figure 4b gives phase diagrams for (PS-2)/($PB^{1,4}$-26H), (PS-2)/($PEB^{1,4}$-26H), and (PVCH-2)/($PEB^{1,4}$-26H) blends, where $PB^{1,4}$-26H refers to a PB with predominantly (74%) 1,4-addition.[12] In Figure 4a, we observe that among the three blend systems (PS-6)/($PEP^{1,4}$-5) blends have the highest critical temperature (T_c) of 189 °C, (PVCH-6)/($PEP^{1,4}$-5) blends have T_c = 165 °C, and (PS-6)/($PI^{1,4}$-5) blends have the lowest T_c, 151 °C. In Figure 4b, we observe that among the three blend systems (PS-2)/($PEB^{1,4}$-26H) blends have the highest T_c of 224 °C, (PVCH-2)/($PEB^{1,4}$-26H) blends have T_c = 143 °C, and (PS-2)/($PB^{1,4}$-26H) blends have the lowest T_c, 118 °C. It is then clear that (PS-6)/($PEP^{1,4}$-5) and (PS-2)/($PEB^{1,4}$-26H) blends have much higher T_c than (PVCH-6)/($PEP^{1,4}$-5) and (PVCH-2)/($PEB^{1,4}$-26H) blends, which in turn have T_c higher than (PS-6)/($PI^{1,4}$-5) and (PS-2)/($PB^{1,4}$-26H) blends. What is of great interest in Figure 4 is that the T_c of (PS-6)/($PEP^{1,4}$-5) blends is 24 °C higher than that of (PVCH-6)/($PEP^{1,4}$-5) blends, while the T_c of (PS-2)/($PEB^{1,4}$-26H) blends is 81 °C higher than that of (PVCH-2)/($PEB^{1,4}$-26H) blends. This observation is consistent with that made above for the T_{ODT} of PS−$PEP^{1,4}$-10/9 and the T_{ODT} of PS−$PEB^{1,4}$-14/11.

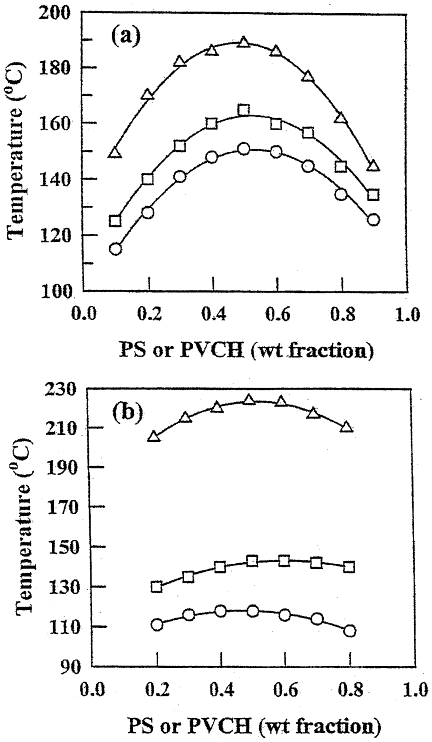

Figure 4. (a) Phase diagrams for (○) (PS-6)/($PI^{1,4}$-5) blends with T_c = 151 °C, (△) (PS-6)/($PEP^{1,4}$-5) blends with T_c = 189 °C, and (□) (PVCH-6)/($PEP^{1,4}$-5) blends with T_c = 165 °C. (b) Phase diagrams for (○) (PS-2)/($PB^{1,4}$-26H) blends with T_c = 118 °C, (△) (PS-2)/($PEB^{1,4}$-26H) blends with T_c = 224 °C, and (□) (PVCH-2)/($PEB^{1,4}$-26H) blends with T_c = 143 °C. The solid lines are drawn through the data points to guide the eyes.

3.2. Prediction of the T_{ODT}s of Completely Saturated PVCH-*block*-PEB and PVCH-*block*-PEP Copolymers, Partially Saturated PS-*block*-PEB and PS-*block*-PEP Copolymers, and the Unsaturated Precursors. To predict the T_{ODT}s of completely saturated PVCH-*block*-PEB and PVCH-*block*-PEP copolymers, partially saturated PS-*block*-PEB and PS-*block*-PEP copolymers, and the unsaturated precursors synthesized in this study via the Leibler theory,[4] we employed the following form of the interaction parameter α (having the units of mol/cm^3)

$$\alpha = a + b/T + c\phi_1/T \tag{1}$$

where *a*, *b*, and *c* are constants, ϕ_1 is the volume fraction of component 1, and *T* is the absolute temperature, which was obtained by curve-fitting the experimental phase diagrams[12] to the theoretical phase diagrams based on the Flory−Huggins theory. Note that the Flory−Huggins interaction parameter χ is related to α

Table 3. Interaction Parameters for PS/PI, PS/PEP, PVCH/PEP, PS/PB, PS/PEB, and PVCH/PEB Pairs Determined from Cloud Point Measurement[12]

sample code	interaction parameter α (mol/cm^3)[a]	eq no.
(a) PS/PI^{1,4}, PS/PEP^{1,4}, and PVCH/PEP^{1,4} blends		
(PS-6)/(PI^{1,4}-5)	$\alpha = -0.1261 \times 10^{-2} + 0.6497/T + 0.0168\phi_{PS}/T$	2
(PS-6)/(PEP^{1,4}−5)	$\alpha = -0.1008 \times 10^{-2} + 0.6066/T - 0.0431\phi_{PS}/T$	3
(PVCH-6)/(PEP^{1,4}-5)	$\alpha = -0.9884 \times 10^{-3} + 0.5587/T - 0.0333\phi_{PVCH}/T$	4
(b) PS/PI^{3,4}, PS/PEP^{3,4}, and PVCH/PEP^{3,4} blends		
(PS-2)/(PI^{3,4}-6)	$\alpha = -0.2904 \times 10^{-2} + 1.6081/T - 0.0576\phi_{PS}/T$	5
(PS-2)/(PEP^{3,4}-6)	$\alpha = -0.1899 \times 10^{-2} + 1.2780/T - 0.2133\phi_{PS}/T$	6
(PVCH-10)/(PEP^{3,4}-6)	$\alpha = -0.1085 \times 10^{-2} + 0.5660/T - 0.0057\phi_{PVCH}/T$	7
(c) PS/PB^{1,4}, PS/PEB^{1,4}, and PVCH/PEB^{1,4} blends		
(PS-2)/(PB^{1,4}-26H)	$\alpha = -0.5345 \times 10^{-2} + 2.4001/T - 0.1306\phi_{PS}/T$	8
(PS-2)/(PEB^{1,4}-26H)	$\alpha = -0.2663 \times 10^{-2} + 1.6867/T - 0.1020\phi_{PS}/T$	9
(PVCH-2)/(PEB^{1,4}-26H)	$\alpha = -0.4693 \times 10^{-2} + 2.1798/T + 0.0154\phi_{PVCH}/T$	10
(PVCH-10)/(PEB^{1,4}-26H)	$\alpha = -0.2419 \times 10^{-2} + 1.1734/T + 0.0887\phi_{PVCH}/\mathrm{T}$	11
(d) PS/PB^{1,2}, PS/PEB^{1,2}, and PVCH/PEB^{1,2} blends		
(PS-2)/(PB^{1,2}-84H)	$\alpha = -0.2076 \times 10^{-2} + 1.1182/T - 0.0051\phi_{PS}/T$	12
(PS-2)/(PEB^{1,2}-84H)	$\alpha = -0.3020 \times 10^{-2} + 1.7457/T - 0.0847\phi_{PS}/T$	13
(PVCH-10)/(PEB^{1,2}-84H)	$\alpha = -0.1028 \times 10^{-2} + 0.5097/T + 0.0069\phi_{PVCH}/T$	14

[a] The Flory−Huggins interaction parameter χ is related to α by $\chi = V_r\alpha$ with V_r being the molar volume of reference component.

by $\chi = V_r\alpha$, with V_r being the molar volume of reference component. The readers are referred to the literature[3] that describes the rationale behind the choice of the form given by eq 1.

Table 3 gives the expressions of α for completely saturated polymer pairs (PVCH/PEP^{1,4}, PVCH/PEP^{3,4}, PVCH/PEB^{1,4}, and PVCH/PEB^{1,2}), partially saturated polymer pairs (PS/PEP^{1,4}, PS/PEP^{3,4}, PS/PEB^{1,4}, and PS/PEB^{1,2}), and the unsaturated precursors (PS/PI^{1,4}, PS/PI^{3,4}, PS/PB^{1,4}, and PS/PB^{1,2}). Referring to Table 3, PB^{1,4}-26H refers to a PB with 74% 1,4-addition and PB^{1,2}-84H refers to a PB with 84% 1,2-addition. The molecular weights of all polymers listed in Table 3 are given in our previous paper.[12] Since the Leibler theory requires the Flory−Huggins interaction parameter χ, values of χ were calculated using the following expression for V_r:

$$V_r = [([\mathrm{M}]_1 v_1)([\mathrm{M}]_2 v_2)]^{1/2} \tag{15}$$

where $[\mathrm{M}]_1$ and $[\mathrm{M}]_2$ are the monomeric molecular weights of components 1 and 2, respectively, and v_1 and v_2 are the specific volumes of components 1 and 2, respectively. Since the specific volume varies with temperature, we used the expressions, given in Table 4, for the specific volumes of PS, PI, PB, PEB, PEP, and PVCH. We hasten to point out that there are other ways of defining V_r, which would then affect predicted values of T_{ODT}.

We wish to point out that the predicted T_{ODT} of a block copolymer is very sensitive to the choice of the expressions for χ (or α); i.e., different values of T_{ODT} may be predicted when using different expressions for the interaction parameter. It is appropriate to mention at this juncture that while the expressions for α summarized in Table 3 were obtained using binary blends, extending the lattice cluster theory[19,20] Freed and co-workers[21,22] have shown that the χ for a block copolymer would not be the same as that for the corresponding binary blends because end effects associated with junction point in diblock copolymer chains might play an important role in the determination of the segment−segment interaction parameter for diblock copolymers. According to Freed and co-workers,[21,22] the differences in χ between the blend and diblock copolymer are manifested by the opposite temperature dependence when polymerization index N is included in obtaining the following form of expression

$$\chi = (a + b/N) + (c + d/N)/T \tag{16}$$

where a, b, c, and d are constants and T is the absolute temperature; i.e., they emphasized the importance of including molecular weight in the expression for χ. Notice that eq 16 reduces to eq 1 for very large values of N without having the composition-dependent term. Our calculation indicates that the contribution of the composition-dependent term to χ is negligibly small for all intents and purposes. In our previous paper,[12] we mentioned the practical difficulty with measuring cloud points for PS/PI pairs, for example (see Figure 1 in ref 12), having very high molecular weights, which would enable us to determine values of a, b, c, and d appearing in eq 16. Therefore, the discussion below should be regarded as being qualitative; i.e., our purpose here is to focus on the general trend describing the effect of segment−segment interaction parameters on the prediction of T_{ODT}s of PVCH-*block*-PEB, PVCH-*block*-PEP, PS-*block*-PEB, and PS-*block*-PEP copolymers with respect to the T_{ODT}s of the unsaturated precursors, as summarized in Table 2.

Table 4. Expressions for the Specific Volumes of PS, PI, PB, PEB, PEP, and PVCH Employed for the Calculation of Reference Volume v_r

material	specific volume v (cm^3/g)	ref
PS	$v_{PS} = 0.9217 + 5.412 \times 10^{-4}(T - 273) + 1.687 \times 10^{-7}(T - 273)^2$	18
PI	$v_{PI} = 1.0771 + 7.22 \times 10^{-4}(T - 273) + 2.46 \times 10^{-7}(T - 273)^2$	15c
PB^{1,2}	$v_{PB} = 1.1072 + 8.19 \times 10^{-4}(T - 273)$	3
PB^{1,4}	$v_{PB} = 1.1138 + 8.24 \times 10^{-4}(T - 273)$	3
PEB	$v_{PEB} = 1.134 + 7.003 \times 10^{-4}(T - 273)$	3
PEP	$v_{PEP} = 1.2061 + 9.69 \times 10^{-4}(T - 406)$	12
PVCH	$v_{PVCH} = 1.0084 + 6.541 \times 10^{-4}(T - 273)$	12

(a) Predicted T_{ODT}s of SB Diblock Copolymers, PS-*block*-PEB and PVCH-*block*-PEB Copolymers. It is seen in Table 2 that the predicted T_{ODT} of PVCH−PEB^{1,4}-14/11 is moderately (ca. 27 °C) higher than that of the unsaturated precursor, while the measured T_{ODT} of PVCH−PEB^{1,4}-14/11 is much higher (>126 °C) than that of the unsaturated precursor. At present we cannot explain the source(s) for such a large difference between the measured T_{ODT} and predicted T_{ODT} for PVCH−PEB^{1,4}-14/11. The prediction of T_{ODT} for SB^{1,4}-14/11 is made using the expression for α given by eq 8 in Table 3, and the prediction of T_{ODT} for PVCH−PEB^{1,4}-14/11 is made using the expression for α given by eq 10 in Table 3, where both eqs 8 and 10 were obtained with comparable molecular weights of the constituent components.[12] Further, in Table 2 we observe that the predicted T_{ODT} of PS−PEB^{1,4}-14/11 is considerably higher (ca. 230 °C) than that of the unsaturated precursor, SB^{1,4}-14/11, and also is much higher (ca. 200 °C) than that of PVCH−PEB^{1,4}-14/11. What is of great interest here is that the predicted T_{ODT} of PVCH-*block*-PEB copolymer is increased over that of the unsaturated precursor when PB block in an SB diblock copolymer has predominantly 1,4-addition. These predictions are in qualitative agreement with experimental results.

Referring to Table 2, the prediction of the T_{ODT} of PVCH−PEB^{1,2}-7/16 is made using the expression for α given by eq 14 in Table 3, while the prediction of the T_{ODT} of SB^{1,2}-7/16 is made using the expression for α given by eq 12 in Table 3, where eq 14 was obtained from (PVCH-10)/(PEB^{1,2}-84H) blends and eq 12 was obtained from (PS-2)/(PB^{1,2}-84H) blends. This is because (PVCH-2)/(PEB^{1,2}-84H) pair was found to be completely miscible over the entire range of blend compositions,[12] and thus it was not possible to obtain, via cloud point measurement, an expression of α for (PVCH-2)/(PEB^{1,2}-84H) blends. On the other hand, (PS-10)/(PB^{1,2}-84H) blends were found to be so strongly immiscible, giving rise to a critical temperature that exceeded the temperature at which thermal degradation/cross-linking reactions began,[12] such that it was not possible in practice to use comparable molecular weights of the constitutive components to obtain the expressions for α (or χ) for PVCH−PEB^{1,2}-7/16 and SB^{1,2}-7/16, respectively.[12] Thus, rigorously speaking, the T_{ODT} of PVCH−PEB^{1,2}-7/16 predicted with eq 14 should not be compared with the T_{ODT} of SB^{1,2}-7/16 predicted with eq 12 because eqs 12 and 14 were *not* obtained using comparable molecular weights of the constituent components.[12] Nevertheless, the use of eq 14 predicts the T_{ODT} of PVCH−PEB^{1,2}-7/16 to be 97 °C, which lies below the glass transition temperature ($T_g = 120$ °C) of PVCH-10. This observation suggests that the Leibler theory predicts PVCH−PEB^{1,2}-7/16 to be in the disordered state, which is in agreement with the experimental result. Notice further in Table 2 that the predicted T_{ODT} of PS−PEB^{1,2}-7/16 is much higher (ca. 160 °C) than that of the unsaturated precursor, SB^{1,2}-7/16, and is considerably higher than that of PVCH−PEB^{1,2}-7/16. What is of great interest here is that the predicted T_{ODT} of PVCH-*block*-PEB copolymer is increased over that of the unsaturated precursor when PB block in an SB diblock copolymer has predominantly 1,4-addition, while the predicted T_{ODT} of PVCH-*block*-PEB copolymer is decreased from that of the unsaturated precursor when PB block in an SB diblock copolymer has predominantly 1,2-addition. That is, the microstructure of PB block in an SB diblock copolymer has a pronounced influence on the predicted T_{ODT} of completely saturated PVCH-*block*-PEB copolymer. These predictions are in qualitative agreement with experimental results. We can then conclude that the segment−segment interaction parameters for PVCH/PEB and PS/PEB blends, which were determined from cloud point measurements, are very useful to explain the effect of the microstructures of PB block in an SB diblock copolymer on the T_{ODT}s of PVCH-*block*-PEB and PS-*block*-PEB copolymers.

(b) Predicted T_{ODT}s of SI Diblock Copolymers, PS-*block*-PEP and PVCH-*block*-PEP Copolymers. It is seen in Table 2 that the predicted T_{ODT} of PVCH−PEP^{1,4}-10/9 is ca. 7 °C higher than that of the unsaturated precursor SI^{1,4}-10/9, and the predicted T_{ODT} of PS−PEP^{1,4}-10/9 is much higher (ca. 21 °C) than that of SI^{1,4}-10/9. At present, we cannot explain the source(s) for such a large difference between the measured T_{ODT} and predicted T_{ODT} for PS−PEP^{1,4}-10/9. The predictions of T_{ODT} for SI^{1,4}-10/9 are made using the expression for α given by eq 2 in Table 3, and the predictions of T_{ODT} for PVCH−PEP^{1,4}-10/9 are made using the expression for α given by eq 4 in Table 3, where both eqs 2 and 4 were obtained with comparable molecular weights of the constituent components.[12] Thus, we can conclude that the general trend of the theoretical prediction of T_{ODT} for PVCH-*block*-PEP^{1,4} copolymers and the unsaturated precursors with predominantly 1,4-addition in the PI block is in line with experimental results.

Referring to Table 2, the prediction of the T_{ODT} of PVCH−PEP^{3,4}-10/10 is made using the expression for α given by eq 7 in Table 3, while the prediction of the T_{ODT} of SI^{3,4}-10/10 with predominantly vinyl content is made using the expression for α given by eq 5 in Table 3, where eq 7 was obtained from (PVCH-10)/(PEP^{3,4}-6) blends and eq 5 was obtained from (PS-2)/(PI^{3,4}-6) blends. This is because the (PVCH-2)/(PEP^{3,4}-6) pair was found to be completely miscible over the entire range of blend compositions, and thus it was not possible to obtain, via cloud point measurement, an expression of α for (PVCH-2)/(PEP^{3,4}-6) blends.[12] On the other hand, (PS-10)/(PI^{3,4}-6) blends were found to be strongly immiscible, giving rise to a critical temperature that exceeded the temperature at which thermal degradation/cross-linking reactions began[12] such that it was not possible in practice to use comparable molecular weights of the constitutive components to obtain the expressions of α (or χ) for PVCH−PEP^{3,4}-10/10 and SI^{3,4}-10/10, respectively.[12] Thus, rigorously speaking, the T_{ODT} of PVCH−PEP^{3,4}-10/10 predicted with eq 7 should not be compared with the T_{ODT} of SI^{3,4}-10/10 predicted with eq 5 because eqs 5 and 7 were *not* obtained using comparable molecular weights of the constituent components.[12] Nevertheless, the use of eq 7 predicts the T_{ODT} of PVCH−PEP^{3,4}-10/10 to be 91 °C, which lies below the glass transition temperature ($T_g = 120$ °C) of PVCH10. The above observations suggest that the Leibler theory predicts PVCH−PEP^{3,4}-10/10 to be in the disordered state, which is in agreement with experimental results. Notice in Table 2 that the predicted T_{ODT} of PS−PEP^{3,4}-10/10 is ca. 25 °C higher than that of the unsaturated precursor SI^{3,4}-10/10 and is considerably higher than that of PVCH−PEP^{3,4}-10/10. What is of great interest here is that the predicted T_{ODT} of PVCH-*block*-PEP copolymer is increased over that of the unsaturated precursor when PI block in an SI diblock copolymer has predominantly 1,4-addition, while the predicted T_{ODT} of PVCH-*block*-PEB copolymer is decreased from that of the unsaturated precursor when PI block in an SI diblock copolymer has predominantly vinyl content. That is, the microstructure of PI block in an SI diblock copolymer has a pronounced influence on the predicted T_{ODT} of completely saturated PVCH-*block*-PEP copolymer. These predictions are in qualitative agreement with experimental results. We can then conclude that the segment−segment interaction parameters for PVCH/PEP and PS/PEP blends, which were determined from cloud point measurements, are very useful to explain the effect of the microstructures of PI block in an SI diblock copolymer on the T_{ODT}s of PVCH-*block*-PEP and PS-*block*-PEP copolymers.

3.3. Conformational Asymmetry Parameter ϵ vs Segment−Segment Interaction Parameter χ for

Block Copolymers: Effect of Microstructure of Polydiene Block. Earlier, Gehlsen and Bates[9] used conformational asymmetry parameter ϵ to explain an experimentally observed increase or decrease in the T_{ODT} of PVCH-*block*-PEB and PVCH-*block*-PEP copolymers with respect to the unsaturated precursors. They defined ϵ by

$$\epsilon = (\beta_1/\beta_2)^2 \tag{17}$$

where $\beta^2 = b/6v_0$ with b being the statistical segment length and v_0 being the segment volume.

The last two columns of Table 2 provide values of ϵ at 150 °C, as estimated from the values of β for PS, PVCH, PI^{1,4}, PB^{1,2}, PB^{1,4}, PEP^{1,4}, PEB^{1,2}, and PEB^{1,2} given in Table 1 of ref 9, and values of α at 150 °C that are calculated from the temperature-dependent expressions for α given in Table 3. It is seen in Table 2 that ϵ increases from 1.59 to 2.08 as SB^{1,4}-14/11 is partially saturated to PS$-$PEB^{1,4}-14/11 and ϵ increases further to 2.28 as SB^{1,4}-14/11 is completely saturated to PVCH$-$PEB^{1,4}-14/11, whereas the α of PS$-$PEB^{1,4}-14/11 is much higher than that of SB^{1,4}-14/11 and PVCH$-$PEB^{1,4}-14/11. A similar observation can be made for SI^{1,4}-10/9, PS$-$PEP^{1,4}-10/9, and PVCH$-$PEP^{1,4}-10/9; ϵ increases from 1.22 to 1.33 as SI^{1,4}-10/9 is partially saturated to PS$-$PEP^{1,4}-10/9, and ϵ increases further to 1.45 as SI^{1,4}-10/9 is completely saturated to PVCH$-$PEP^{1,4}-10/9, whereas the α of PS$-$PEP^{1,4}-10/9 is higher than that of SI^{1,4}-10/9 and PVCH$-$PEP^{1,4}-10/9. On the other hand, it is seen in Table 2 that ϵ decreases monotonically from 1.26 to 1.10 as SB^{1,2}-7/16 is partially saturated to PS$-$PEB^{1,2}-7/16 and completely saturated to PVCH$-$PEB^{1,2}-7/16, whereas α of PS$-$PEB^{1,2}-7/16 is much higher than that of SB^{1,2}-7/16 and PVCH$-$PEB^{1,2}-7/16. Thus, we conclude that apparently there is no correlation between ϵ and α for *partially* saturated block copolymers: PS$-$PEB^{1,4}-14/11, PS$-$PEP^{1,4}-10/9, and PS$-$PEB^{1,2}-7/16.

We now address a more fundamental issue: Can the difference in conformational asymmetry between SB^{1,2} and SB^{1,4} explain the effect of microstructure on the T_{ODT} of the two block copolymers? Since the T_{ODT} of a block copolymer depends on molecular weight and block composition,[4,5] it is essential for one to use two block copolymers, SB^{1,2} and SB^{1,4}, that have an identical molecular weight and also an identical block composition to investigate the effect of microstructure on T_{ODT}. For this, in this study we synthesized two additional SB diblock copolymers, SB^{1,4}-12/12 and SB^{1,2}-11/11, the molecular characteristics of which are summarized in Table 1. It is practically very difficult, if not impossible, to have identical molecular weight and also identical block composition by conducting two separate polymer syntheses: an SB^{1,4} diblock copolymer was synthesized in cyclohexane as solvent, and an SB^{1,2} diblock copolymer was synthesized in cyclohexane as solvent in the presence of bis(piperidino)ethane as a polar additive.[23] Notice in Table 2 that the molecular weight of SB^{1,4}-12/12 is slightly higher than that of SB^{1,2}-11/11.

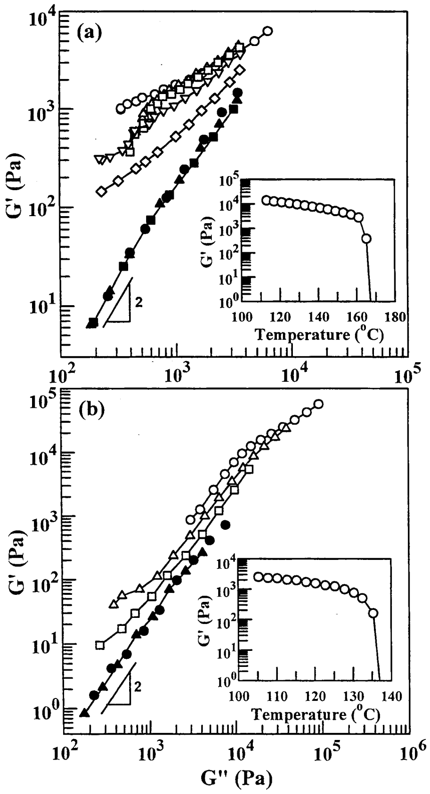

Figure 5. (a) Plots of log G' vs log G'' for SB^{1,2}-11/11 at various temperatures: (○) 110, (△) 130, (□) 150, (▽) 160, (◇) 165, (●) 170, (▲) 175, and (■) 180 °C. (b) Plots of log G' vs log G'' for SB^{1,4}-12/12 at various temperatures: (○) 110, (△) 120, (□) 130, (●) 140, and (▲) 150 °C. The inset on each panel gives the results of the isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s.

Figure 5a gives log G' vs log G'' plots for SB^{1,2}-11/11 at various temperatures during heating, indicating that the T_{ODT} of this block copolymer lies between 165 and 170 °C, while the results of the isochronal dynamic temperature sweep experiment at $\omega = 0.1$ rad/s given in the inset indicates that T_{ODT} is ca. 168 °C. Since the temperature increment in the log G' vs log G'' plots is 5 °C, below we will regard 168 °C as the T_{ODT} of SB^{1,2}-11/11. Figure 5b gives log G' vs log G'' plots for SB^{1,4}-12/12 at various temperatures during heating, indicating that the T_{ODT} of this block copolymer is ca. 135 °C. It is clear from Figures 5 that the T_{ODT} of SB^{1,2}-11/11 is ca. 33 °C higher than that of SB^{1,4}-12/12 although the molecular weight of SB^{1,2}-11/11 is slightly lower than that of SB^{1,4}-12/12. It is well established that T_{ODT} increases with an increase in molecular weight for block copolymers having the same chemical structure.[4,5] Thus, we can conclude that an SB diblock copolymer with predominantly 1,2-addition in the PB block has a higher T_{ODT} than an SB diblock copolymer with predominantly 1,4-addition in the PB block.

Table 5 gives a summary of measured and predicted T_{ODT}s, together with the values of ϵ and α at 150 °C, for SB^{1,2}-11/11 and SB^{1,4}-12/12. Also given in Table 5 are, for comparison, the experimental results of Gehlsen and Bates[9] who measured the T_{ODT}s of two SB diblock copolymers: 1,2-PB$-$PS-1 that has 99% 1,2-addition in the PB block and 1,4-PB$-$PS-2 that has 93% 1,4-addition in the PB block, both having molecular weights and block compositions that are reasonably close to each other. It is seen in Table 5 that the T_{ODT} of 1,2-PB$-$PS-1 is much higher ($>$108 °C) than that of 1,4-PB$-$PS-2, which is in agreement with our experimental results for SB^{1,2}-11/11 and SB^{1,4}-12/12. It is clear from Table 5 that the value of ϵ for SB^{1,2}-11/11 (or 1,2-PB$-$PS-1) is smaller than that of SB^{1,4}-12/12 (or 1,4-PB$-$PS-2), showing a trend opposite to that of the measured T_{ODT}, whereas the value of α for SB^{1,2}-11/11 (or 1,2-PB$-$PS-1) is larger than that for SB^{1,4}-12/12 (or 1,4-PB$-$PS-2), showing the same trend as the measured T_{ODT} does.

Table 5. Summary Describing the Effect of the Microstructures of Polybutadiene Block in SB Diblock Copolymers on T_{ODT}, ϵ, and α

sample code	$M_n \times 10^{-3}$	wt frac of PS	measured T_{ODT} (°C)	predicted T_{ODT} (°C)[a]	ϵ^b (150 °C)	$\alpha \times 10^3$ (150 °C)
			(a) This Study			
$SB^{1,2}$-11/11[c]	22.5	0.50	168	171	1.26	0.890
$SB^{1,4}$-12/12[d]	23.8	0.50	135	134	1.58	0.599
			(b) Gehlsen and Bates[9]			
1,2-PB−PS-1	22	0.54	>275	176	1.26	0.890
1,4-PB−PS-2	20	0.51	167	118	1.58	0.599

[a] Estimated from the Leibler theory. [b] Estimated from Table 1 of ref 9. [c] $T_{g,PS}$ = 61 °C; thus, the measured T_{ODT} of this block copolymer is ca. 107 °C higher than its $T_{g,PS}$. [d] $T_{g,PS}$ = 65 °C; thus, the measured T_{ODT} of this block copolymer is ca. 70 °C higher than its $T_{g,PS}$.

Table 6. Interaction Parameters Determined from Cloud Point Measurements for Binary Blends of Polystyrene and Polybutadiene with Varying Microstructures[3]

sample code	microstructure (wt %)	interaction parameter α (mol/cm³)	$\alpha \times 10^3$ (150 °C)	eq no.
(PS-2)[a]/(PB-1)[b]	7% 1,2-addition	$\alpha = -0.163 \times 10^{-2} + 0.944/T + 0.008\phi_{PS}/T$	0.599	18
(PS-2)[a]/(PB-2)[c]	50% 1,2-addition	$\alpha = -0.158 \times 10^{-2} + 1.003/T - 0.034\phi_{PS}/T$	0.793	19
(PS-2)[a]/(PB-3)[d]	78% 1,2-addition	$\alpha = -0.189 \times 10^{-2} + 1.178/T - 0.053\phi_{PS}/T$	0.890	20

[a] PS-2 has $M_w = 1.5 \times 10^3$ and $M_w/M_n = 1.1$ as determined by gel permeation chromatography (GPC). [b] PB-1 has 7 wt % 1,2-addition as determined by ^{1}H NMR spectroscopy, and $M_w = 3793$ and $M_w/M_n = 1.02$ as determined by mass spectral (MS) analysis. [c] PB-2 has 50 wt % 1,2-addition as determined by ^{1}H NMR spectroscopy, and $M_w = 3674$ and $M_w/M_n = 1.02$ as determined by MS analysis. [d] PB-3 has 78 wt % 1,2-addition as determined by ^{1}H NMR spectroscopy, and $M_w = 4191$ and $M_w/M_n = 1.02$ as determined by MS analysis.

It is seen in Table 5 that apparently the conformational asymmetry parameter ϵ does not explain the effect of microstructures of unsaturated SB diblock copolymer on T_{ODT}, while the interaction parameter α does.

Figure 6 gives phase diagrams, which were obtained from cloud point measurement, of three PS/PB blends with varying microstructures of PB: a phase diagram of PS/(PB-1) blends with 7% 1,2-addition (thus predominantly 1,4-addition) in PB (○), a phase diagram of PS/(PB-2) blends with 50% 1,2-addition in PB (△), and a phase diagram of PS/(PB-3) blends with 78% 1,2-addition (thus predominantly 1,2-addition) in PB (□), where PS has $M_w = 1.5 \times 10^3$, PB-1 has $M_w = 3.8 \times 10^3$, PB-2 has $M_w = 3.7 \times 10^3$, and PB-3 has $M_w = 4.1 \times 10^3$, all having a very narrow molecular weight distribution. It is seen in Figure 6 that the phase diagram moves upward as the 1,2-addition content in PB increases from 7 to 78%, indicating that the miscibility of PS/PB pair decreases with increasing 1,2-addition content in PB. From this observation we expect that the T_{ODT} of SB diblock copolymer will increase with increasing 1,2-addition content in PB block. The experimental results summarized in Table 5 meet with this expectation.

By curve fitting the phase diagrams given in Figure 6 to the theoretical phase diagrams from the Flory−Huggins theory, temperature-dependent segment−segment interaction parameter α was determined for each blend system, and the results are summarized in Table 6. Also given in Table 6 are values of α at 150 °C for the three blend systems, in which we observe that α *increases* with increasing 1,2-addition content in PB. Note that α can be regarded as representing, although indirectly, the chemical structures of the constituent components of a polymer blend or a block copolymer. In this context, α is expected to reflect consistently on the differences in T_{ODT} between $SB^{1,2}$ and $SB^{1,4}$ diblock copolymers and also on the differences in phase behavior between $PS/PB^{1,2}$ and $PS/PB^{1,4}$ blends. Notice in Figure 6 that the critical temperature (T_c) of PS/PB blends increases with increasing 1,2-addition content in PB. This observation is consistent with that made above for the $SB^{1,2}$-11/11 and $SB^{1,4}$-12/12 diblock copolymers (see Table 5) in that the T_{ODT} of $SB^{1,2}$-11/11 with predominantly 1,2-addition in the PB block is higher than that of $SB^{1,4}$-12/12 with predominantly 1,4-addition in the PB block. In other words, all three quantities, α, T_c, and T_{ODT}, move in the same direction as the microstructure of PB in a PS/PB binary blend or the microstructure of the PB block in an SB diblock copolymer varies. According to Gehlsen and Bates,[9] $\epsilon = 1.3$ for $SB^{1,2}$ and $\epsilon = 1.6$ for $SB^{1,4}$ (also see Table 5); i.e., ϵ moves in the direction which is opposite to the direction T_{ODT} moves as the microstructure of the PB block in an SB diblock copolymer varies. Thus, we conclude that conformational asymmetry does *not* explain the effect of microstructure of the PB block in an SB diblock copolymer on T_{ODT}, while the segment−segment interaction parameter can.

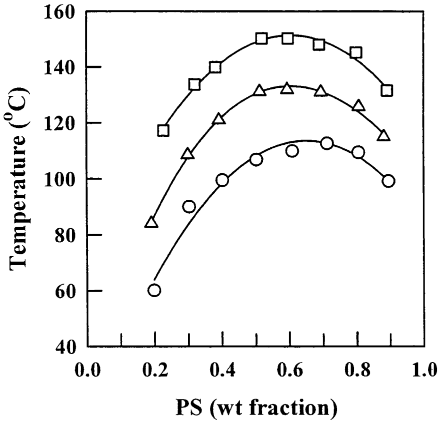

Figure 6. Phase diagrams for (○) (PS-2)/(PB-1) blends, (△) (PS-2)/(PB-2) blends, and (□) (PS-2)/(PB-3) blends, where PS-2 has $M_w = 1.5 \times 10^3$ from MS analysis, PB-1 with 7 wt % 1,2-addition has $M_w = 3793$ from MS analysis, PB-2 with 50 wt % 1,2-addition has $M_w = 3674$ from MS analysis, and PB-3 with 78 wt % 1,2-addition has $M_w = 4191$ from MS analysis. The solid lines are drawn through the data points to guide the eyes.

4. Concluding Remarks

In this study, we synthesized a series of SB and SI diblock copolymers with varying microstructures of polydiene blocks, and subsequently they were either partially saturated, yielding PS-*block*-PEB or PS-*block*-PEP copolymers, or completely saturated, yielding PVCH-*block*-PEB or PVCH-*block*-PEP copolymers. We have found that the T_{ODT} of completely saturated PVCH-*block*-PEB or PVCH-*block*-PEP copolymers is higher than that of the unsaturated precursors with predominantly 1,4-addition in the PB or PI block and lower than that of the unsaturated precursors with predominantly vinyl content in the PB or PI block. However, the T_{ODT} of partially saturated PS-*block*-PEB or PS-*block*-PEP copolymers is significantly higher than that of completely saturated PVCH-*block*-PEB or PVCH-*block*-PEP copolymers and, also, higher than that of the unsaturated precursors, irrespective of the microstructures of polydiene block.

Variations in T_{ODT} of both partially saturated PS-*block*-PEB and PS-*block*-PEP copolymers and completely saturated PVCH-*block*-PEB or PVCH-*block*-PEP copolymers were assessed using the temperature-dependent segment−segment interaction parameters, which were obtained from cloud point measurements of PS/PB, PS/PI, PS/PEB, PS/PEP, PVCH/PEB, and PVCH/PEP blends with varying microstructures of polydiene. The segment−segment interaction parameters for the total of 13 polymer pairs (see Table 3) were determined by curve fitting the experimental phase diagrams to the theoretical phase diagrams based on the Flory−Huggins theory. We have found that predicted values of T_{ODT} for the block copolymers from the Leibler theory show the same trend as the experimental results although the predicted values of T_{ODT} are much lower than the experimentally determined values. We wish to emphasize that the predicted values of T_{ODT} must be regarded as being approximate for the reason that the segment−segment interaction parameters were obtained using molecular weights which were lower than the molecular weights of the block copolymers. Because cloud point measurements with high molecular weights of polymer pairs were not possible without having thermal degradation/cross-linking reactions, the effect of molecular weight (rigorously speaking, degree of polymerization) of polymer pairs on the segment−segment interaction parameter (see eq 16) could not be included. Note that the predicted T_{ODT} depends on the degree of polymerization.[4,5] Although in this paper we used the Leibler theory[4] to predict the T_{ODT} of block copolymers, other theory (e.g., the Helfand−Wasserman theory[5]) can predict different values of T_{ODT}.[24] The general trend of increasing or decreasing T_{ODT} summarized in Tables 2 and 5, however, will remain the same, regardless of which of the two theories is used to predict the T_{ODT} of the block copolymers. It is then fair to state that mean-field theory is very helpful to gain insight into phase transitions in cylinder- or lamella-forming block copolymers (see Tables 2 and 5).

On the basis of the experimental results obtained from this study, we observe that variations in conformational asymmetry parameter ϵ and interaction parameter α show the same trend as does the T_{ODT} of completely saturated block copolymers, but they do not show the same trend as does the T_{ODT} of partially saturated block copolymers. Thus, we conclude that a correlation between ϵ and χ seems to exist for completely saturated block copolymers but not for partially saturated block copolymers.

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