9074 *Macromolecules* **1999,** *32,* 9074−9077

Microphase Separation in ABC Block Copolymers with a Short but Strongly Interacting Middle Block

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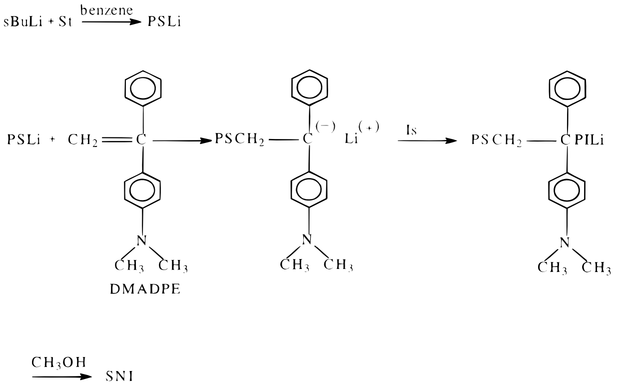
Received August 5, 1999

Introduction. Recent experiments[1] on ABC triblock copolymers revealed new intriguing morphologies not observed with AB diblock or ABA triblock copolymers. Linear ABC triblock copolymer phase behavior is controlled by three interaction parameters, χ_{AB}, χ_{BC}, and χ_{AC}, as opposed to just one in AB diblocks and two independent composition parameters f_A and f_B. In addition, unlike with diblock copolymers, the sequence of blocks, i.e., ABC, ACB, CAB, results in an unparalleled morphological complexity. For example, Stadler and collaborators[2,3] demonstrated the existence of decorated lamellae with cylinders and spheres, rings-on-cylinders, coaxial cylinders, concentric spherical domains in bcc structure, and lately the striking "knitting" pattern with a two-dimensional space group of *c*2*mm*. Although the morphological possibilities in linear ABC and miktoarms[4] have been explored both experimentally and theoretically,[5−7] the effect of the rich parameter space on the order-to-disorder transition and flow regime of the copolymers with implication to processing is relatively unexplored. Recent theoretical efforts[8,9] have treated the case of ABC copolymers bearing a finite or a pointlike central block B. It was found that the size and interactions of the central block play an important role in delineating the miscibility of the AC diblock. A long central block can induce a morphological transition from B cylinders at the AC lamellae interface to cylinders in a mixed AC matrix; i.e., the central B block can enhance the miscibility of the outer blocks. On the other hand, the case of a short but strongly interacting midblock is predicted to have a very different effect on the outer block miscibility. In the case where the outer blocks have a small but finite incompatibility and the inner block is short but strongly interacting (i.e., $\chi_{AC} \neq 0$ and $\chi_{AB}, \chi_{BC} \gg \chi_{AC}$), it is predicted that the critical temperature increases by $^5/_3$ as compared to the AC diblock case.

Here we present the first, to our knowledge, relevant experimental work treating the latter theoretical case by employing junction point functionalized copolymers of polystyrene (PS) and polyisoperene (PI). The functional group is zwitterion (Zw), i.e., a short and strongly interacting ionic group. In the past we reported[10] on the phase state and dynamics of cylinder-forming asymmetrically functionalized diblock copolymers (AC) of the ACB and BAC type with the same functional group B. We found that the zwitterion induces another level of phase separation, namely between the ionic and hydrocarbon materials on top of the segregation between the two hydrocarbon blocks. Furthermore, the presence of the short zwitterionic group leads to stabilization of the ordered structures, and the formation of multiplets within the PS phase and the latter case was also treated theoretically.[11]

Scheme 1



For the structure investigation we used SAXS and rheology. We found that inserting the Zw group within the PS−PI junction decreases the miscibility of the PS−PI diblock in accord with the theoretical predictions. Moreover, at the order-to-disorder transition temperature (T_{ODT}) both the microstructure and the aggregates dissolve. The location of the functional group at the PS−PI junction makes the system suitable for probing the dynamics of the polar group within the interface. For this purpose we have employed dielectric spectroscopy and studied the local, chain, and slow dynamics in the ordered state.

Experimental Section. *Samples.* The junction point functionalized copolymers were synthesized by high-vacuum anionic polymerization techniques. All reagents were purified using well-established anionic polymerization procedures. Polymerizations were performed in all glass *n*-BuLi cleaned and benzene rinsed reactors.[12] Styrene was polymerized first using *sec*-BuLi as initiator. After completion of polymerization a small excess of 1-(4-dimethylaminophenyl)-1-phenylethylene (DMADPE), distilled over *n*-BuLi, was introduced to the reaction mixture (DMADPE/Li = 1.1/1) as shown in Scheme 1. The reaction was left for completion for 3 days at room temperature. Isoprene was then added, and after 24 h the polymerization was terminated by addition of degassed methanol. Polymers were precipitated in methanol and dried under vacuum.

The resulting copolymers were characterized by size exclusion chromatography (SEC), low-angle laser light scattering (LALLS), membrane osmometry (MO), and NMR spectroscopy. The molecular characteristics of the copolymers are given in Table 1. These characterization results indicate a high degree of molecular weight and compositional homogeneity of the samples. The dimethylamino groups were converted to sulfobetaine zwitterions by reaction with excess cyclopropane sultone as shown in Scheme 2. The reaction took place in dilute THF solutions at 343 K for several days to ensure complete conversion.

Small-angle X-ray scattering (SAXS) measurements were performed with a Kratky compact camera (Anton Paar) equipped with a one-dimensional position sensi-

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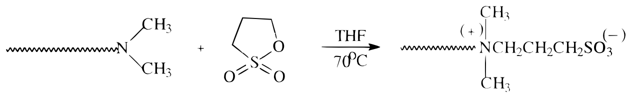
10.1021/ma991316y CCC: $18.00

Table 1. Molecular Characteristics of Junction Point Functionalized Diblock Copolymers

sample	$M_w \times 10^{-4\ a}$	$M_n \times 10^{-4\ b}$	$M_{n,PS} \times 10^{-4\ b}$	wt % PS^c	$M_w/M_n{}^d$	$N^*_{n,PS}{}^e$	$N^*_{n,PI}{}^e$	$f_{PS}{}^g$
SNI-5	6.13	5.52	2.86	50	1.05	314	342	0.48
SNI-1	2.75	2.46	1.13	46	1.04	124	171	0.42
SNI-3	1.80	1.69	0.78	46	1.04	86	117	0.42
SNI-4	1.42	1.28	0.54	42	1.04	71	109	0.39

[a] Low-angle laser light scattering. [b] Membrane osmometry. [c] ^{1}H NMR. [d] Size-exclusion chromatography. [e] Calculated from $N^*_{n,PS} = N_{n,PS}(\rho^*_I/\rho^*_S)^{1/2}$. [f] Caclulated from $N^*_{n,PI} = N_{n,PI}(\rho^*_S/\rho^*_I)^{1/2}$. [g] $f_{PS} = N^*_{n,PS}/(N^*_{n,PS} + N^*_{n,PI})$.

Scheme 2



tive detector (M. Braun). The Ni-filtered Cu Kα radiation ($\lambda = 0.154$ nm) was used from a Siemens generator. Measurements of 1 h long were made within the *T* range 298−433 K with a stability of ±0.1 K. The data were corrected for absorption, background scattering, and slit-length smearing. Intensities were converted to absolute units by using the moving slit method.

Rheology was employed with the use of an advanced rheometric expansion system (ARES), equipped with a force-rebalanced transducer. All experiments were made in the linear viscoelastic range. The first experiment involved measuring the storage (G') and loss (G'') moduli as a function of *T* under isochronal conditions ($\omega = 1$ rad/s) with a heating and cooling rate of 0.5 K/min and a low strain amplitude. In a second experiment we performed isothermal frequency scans at different temperatures below and above the transition. We have then shifted the curves using as a reference the lowest *T* corresponding to the PS glass transition (T_g). In this way we obtained shift factors corresponding to the PS segmental relaxation.

Dielectric spectroscopy (DS) measurements were made with a Novocontrol broad-band dielectric convertor (BDC-S) system composed of a frequency response analyzer (FRA) (Solartron Schlumberger 1260) and a BDC with an active sample cell. Measurements of the complex dielectric function were made in the frequency range 10^{-2}−10^6 Hz and for temperatures in the range from 200 K up to the respective T_{ODT}. The samples were kept between two gold-plated stainless steel plates of 20 mm in diameter with a separation of 100 μm maintained by means of Teflon spacers.

Results and Discussion. All junction point functionalized diblock copolymers formed a lamellar phase[13] as expected from the symmetric composition. Figure 1 gives representative spectra of the SZwI-4 copolymer at temperatures corresponding to the vicinity of the order-to-disorder transition. The spectra exhibit a broad liquidlike peak above the T_{ODT} (~371 K) and a narrower peak at lower temperatures due to segregation in PS- and PI-rich domains. The absence of an additional peak in $S(Q)$ originating from the ionic aggregates, previously seen[10] in the asymmetrically functionalized copolymers ZwIS, is indicative of the smaller aggregation number in the present system presumably because of the steric hindrance of the Zw group with PS and PI.

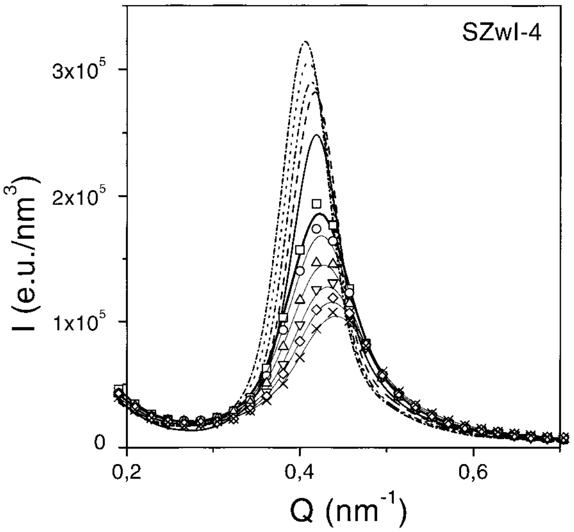


Figure 1. SAXS spectra of the SZwI-4 copolymer shown at some selected temperatures: (dash-dotted line) $T = 348$ K, (dotted line) $T = 353$ K, (dash double-dotted line) $T = 358$ K, (dashed line) $T = 363$ K, (solid line) $T = 367$ K, (□) $T = 371$ K, (○) $T = 374$ K, (△) $T = 378$ K, (▽) $T = 383$ K, (◇) $T = 388$ K, (×) $T = 393$ K. The order-to-disorder transition temperature is at 371 K. Lines are guides for the eye.

In Figure 2 the results from the SAXS investigation are compared for the same copolymers. The inverse peak intensity, peak width, and peak position are discontinuous at the respective transition temperatures (356 and 368 K for the SNI-3 and SZwI-3, respectively). The discontinuity in the $Q^*(T)$ probably arises from the slight asymmetric composition of the diblocks. For the SNI-1 and SZwI-1 copolymers the corresponding transition temperatures are at 413 and 418 K, respectively. Employing only the block copolymers with the same composition (i.e., SNI-3 and SNI-1, $f_{PS} = 0.42$) and the mean-field theory predictions ($\chi N = 10.9$), we obtain the following $\chi(T)$ for SNI and SZwI: $\chi = 43/T - 0.068$ and $\chi = 52/T - 0.086$, respectively, indicating a stronger *T* dependence in the latter. Notice that both enthalpic and entropic contributions to the interaction parameter are modified.

The effect of zwitterion substitution on the viscoelastic response of the block copolymers is shown in Figure 3 for the SNI-3 and SZwI-3 samples. Clearly in the latter system the ordered state viscosity and moduli are higher than in the former. Furthermore, the T_{ODT} increases by about 10 K as indicated by the drop of the moduli at high temperatures in agreement with SAXS.

The results presented in Figures 2 and 3 clearly demonstrate that when a short (pointlike) block B is inserted in the AC junction, the A block having a finite incompatibility with C increases the incompatibility of AC. We should point out here that the degree of association is very small in these diblocks as indicated by SAXS, but even so the midblock is effective in increasing (i) the viscosity and (ii) the T_{ODT}. The results presented here are in qualitative agreement with recent theoretical predictions on the microphase separation transition in ABC block copolymers with a strongly interacting B block.[8] The theory predicts that inserting an infinitely small central B block infinitely incompatible with both side blocks A and C (A and C having a small but finite incompatibility) results in a continuous

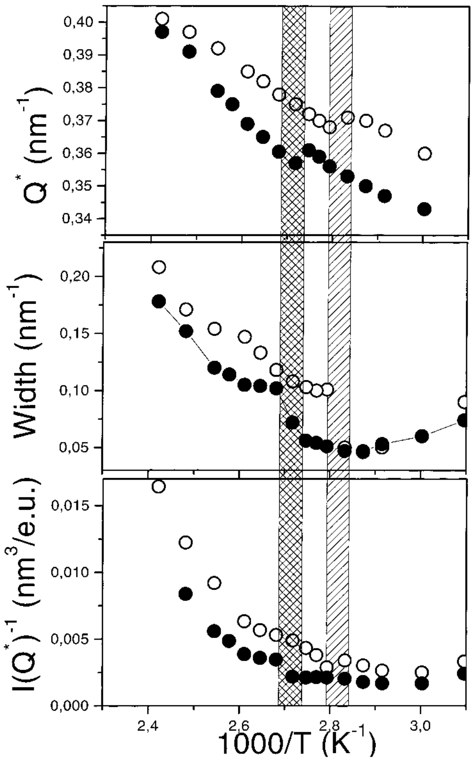


Figure 2. *T* dependence of the first peak of the structure factor (peak position at *Q**, width, and inverse peak intensity) for the SNI-3 (open circles) and the SZwI-3 (filled symbols). The shaded areas indicates the order-to-disorder transition regimes.

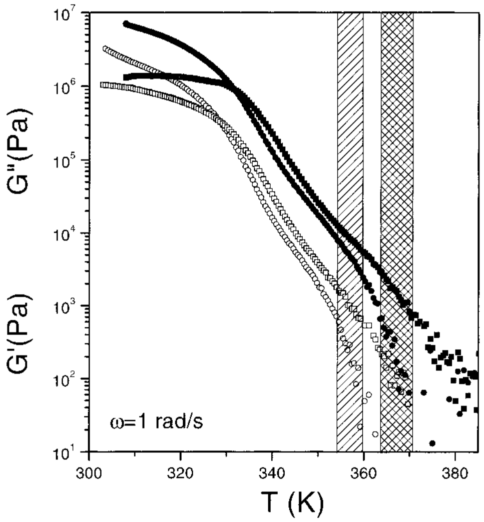


Figure 3. Isochronal ($\omega = 1$ rad/s) temperature runs obtained by heating (heating rate 0.5 K/min) for the storage (circles) and loss (squares) moduli of the SNI-3 (open symbols) and SZwI-3 (filled symbols) copolymers. The shaded area indicate the respective transition regimes.

microphase separation at a temperature $T_{\mathrm{ODT}}{}^{\mathrm{ABC}} = {}^{5}/_{3}T_{\mathrm{ODT}}{}^{\mathrm{AC}}$. However, the increase observed experimentally was only few degrees probably due to the finite incompatibility of B with the AC.

In addition to the structural investigation we have explored the dynamics in the ordered (lamellar) phase with dielectric spectroscopy. A unique property of the present system is that the polar group is situated at the junction point and thus can be used as a dynamic probe of the interface. Furthermore, the method is sensitive to local and global motions in type A polymers (i.e., polymers bearing dipole moment both parallel and perpendicular to the backbone) and in some copolymer architectures can be employed as a dynamic probe of the interfacial width.[14] All dielectric measurements were made in the ordered (lamellar) phase. The method revealed three common relaxations in the SNI and SZwI copolymers, which starting from lower temperatures correspond to (i) the β-relaxation, (ii) the PI segmental relaxation, and (iii) the PI spectrum of normal modes. The results for the characteristic relaxation times corresponding to the different processes are shown in Figure 4 in the usual Arrhenius representation for two copolymers: SNI-4 and SZwI-4. Similar results have been obtained for all copolymers. The β-relaxation relates to the dynamics of the 3,4 units since it is better resolved in the SNI-4 and SZwI-4 copolymers which have the highest content of 3,4 PI units (46%). The line in Figure 4 is a fit to the Arrhenius equation: $\tau = \tau_0 \exp(E/RT)$, where τ_0 is the high-*T* intercept and *E* is the activation energy and results in about 9 kcal/mol, i.e., a typical activation energy for a sub-glass relaxation. All relaxations above T_g exhibit a curvature in Figure 4 and can be fitted to the Vogel–Fulcher–Tammann (VFT) equation: $\log \tau = \log \tau_0 + (B/T - T_\infty)$, where *B* and T_∞ are the apparent activation energy and "ideal" glass transition, respectively. Using the VFT equation, we obtained $-\log(\tau_0/\mathrm{s}) = 13$, $B = 697$ K, $T_\infty = 215$ K for the segmental relaxation of SNI-4 and $-\log(\tau_0/\mathrm{s}) = 13$, $B = 636$ K, $T_\infty = 229$ K for the corresponding relaxation in SZwI-4. The shift in the "ideal" transition temperature reflects the increased glass transition as measured by calorimetry and seen also in Figure 3 from the crossing of the moduli. The longest normal mode—originating from dipole moment along the chain contour—was found to shift to higher *T* by the same amount as the segmental relaxation, indicating local friction effects. The above relaxations are common to type A polymers, and their temperature and pressure dependence has been investigated.[15]

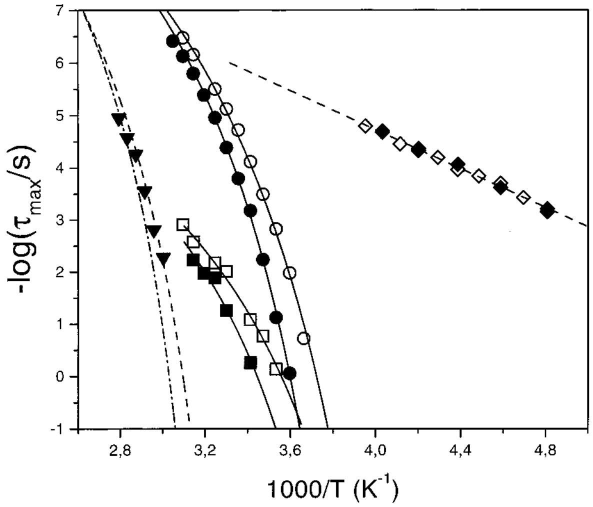


Figure 4. Relaxation map in the usual Arrhenius representation for the NSI-4 (open symbols) and SZwI-4 (filled symbols) copolymers showing four relaxations. Starting from low *T*: (i) sub-glass relaxation (diamonds), (ii) segmental relaxation (circles), (iii) longest normal mode (squares), and (iv) high-*T* relaxation only in the SZwI-4 (inverse triangles). The dashed and dash-dotted lines give respectively the PS shift factors as obtained from rheology (see text) and indicate that the latter relaxation in SZwI-4 originates from aggregates within the PS phase.

However, an additional process at higher temperatures was found only in the functionalized copolymer with shift factors similar to the PS phase but with much higher intensity. The shift factors corresponding to the PS phase (obtained from rheology) are also plotted in Figure 4 with lines. The location and intensity of the mode in the Zw-containing copolymers are consistent with aggregates within the PS phase and could be related to polarizability selectivity and/or to an asymmetric interface. Dielectric spectroscopy provides a dynamic signature of aggregation which gives rise to the increased viscosity and T_{ODT}.

In conclusion, inserting a short but strongly interacting block at the junction decreases the miscibility of the diblock in accord with the theoretical predictions. The location of the functional group facilitates an investigation of the dynamics of the interface using the polar group as a probe. In the future[13] we will report on the effect of Zw substitution on symmetric in composition but asymmetric in functionality diblock copolymers ZwIS, ZwSI and of diblock and triblock copolymers functionalized at both chain ends and junctions, respectively. We will show how the location of the short functional group can affect both the structure factor and dynamics.

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