**Full Paper:** Series of diblock and triblock ionomers based on carboxylated polystyrene-*block*-poly(ethylene-*co*-propylene) (CSEP) and carboxylated polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-styrene) (CSE-BS), i.e., the zinc salts of diblock ZnCSEP and triblock ZnCSEBS were prepared and, respectively, mixed with poly[(butyl methacrylate)-*co*-(4-vinylpyridine)] (BVP) in tetrahydrofuran (THF). It was found that ZnCSEBS/BVP blend solutions exhibit enhanced viscosities and increasing hydrodynamic radii with narrowing distributions in solution, as well as improved glass transition temperature (T_g) of the ionomeric polystyrene (PS) blocks in bulk, which indicates complexation between ZnCSEBS and BVP chains. In contrast, ZnCSEP/BVP blends show viscosities and hydrodynamic radii close to the values calculated from the additivity law, and invariable T_gs of two blocks of ZnCSEP, suggesting that ZnCSEP can not form complexes with BVP. This architectural effect of the block ionomers on their complexation behavior has been interpreted in terms of the difference in structural characters of the associations of the diblock and triblock iono-

mers in solutions formed due to the aggregation of the ionic groups.
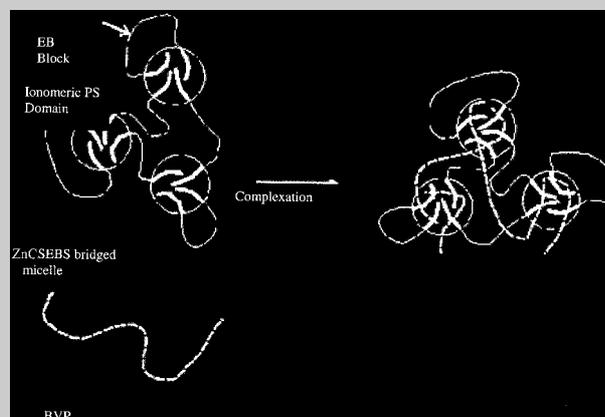
A schematic plot of the complexation of triblock ionomer ZnCSEBS with BVP.

Intermacromolecular Complexation due to Specific Interactions, 14[a]

The Chain Architectural Effect of Block Ionomers on Complexation

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Introduction

There has been a growing interest in polymer-polymer complexation due to secondary bonding or specific interactions such as hydrogen bonding (H-bonding) and ionic interactions, because the resulting complexes have many potential industrial applications and can be used as simplified models providing information about some biological processes.[1–22] The interpolymer complexation due to

H-bonding has been extensively investigated and was reviewed recently.[5] It has been demonstrated that H-bonding complexation generally leads to a decreased viscosity and an increased hydrodynamic radius in solution and only one T_g in bulk.[5] On the other hand, ionic interaction complexation regarding random and telechelic ionomers often shows an increased viscosity in solution and two T_gs in bulk.[10–21]

In recent years, efforts to study the ionic interaction based on complexation have been extended to those com-

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[a] For Part 13 of this series, cf. ref.[38]

plex systems containing block ionomers, which comprise both ionomer and hydrocarbon chains.[22–25] It was reported that both triblock ionomers based on sulfonated SEBS(SSEBS)[22, 23] and sulfonated diblock polystyrene-*block*-poly(ethylene-*co*-propylene) (SSEP)[24, 25] form complexes with polymers containing pyridine units. This leads to an increased hydrodynamic radius, increased viscosity and one T_g in bulk for the blend phase composed of ionomer block and pyridine-containing polymer. However, in the case of carboxylated ionomers, triblock and diblock ionomers show very different complexation behavior. As a part of our research program, the investigation of the complexation and aggregation of block ionomers, this study concentrates on the chain architectural effect of block ionomers on their complexation with pyridine-containing polymers. For this reason, we prepared two series of monodispersed ionomers, i.e., diblock ionomers ZnCSEP and triblock ionomer ZnCSEBS with a common Zn carboxylated polystyrene block. The nonionic blocks, i.e., the ethylene-*co*-propylene (EP) block in the former and ethylene-*co*-butylene (EB) block in the latter are similar in chemical structure.

Experimental Part

Materials

Monodispersed SEP ($\bar{M}_n$ = 1.18 × 10⁵, $\bar{M}_w/\bar{M}_n$ = 1.10 and SEBS ($\bar{M}_n$ = 5.25 × 10⁴, $\bar{M}_w/\bar{M}_n$ ≤ 1.06) were commercially available from Shell Co. with a styrene content of 29.0 wt.-% and 28.6 wt.-%, respectively. CSEP and CSEBS with different carboxylation levels were synthesized by partially carboxylating the PS blocks via a mild Friedel-Crafts acetylation and subsequent haloform oxidation of the resulting acetyl groups with cetyltrimethylammonium bromide as the phase transfer catalyst. As shown in our previous work, this procedure of chemically modifying SEP and SEBS does not affect the monodispersity of the starting materials. The procedure is described in detail elsewhere.[24, 26, 27] CSEP and CSEBS were further converted to block ionomers ZnCSEP and ZnCSEBS by neutralizing the corresponding THF solutions with a 30 wt.-% excess of zinc acetate dihydrate in a toluene/methanol mixture. Complete neutralization was ensured by removing acetic acid by means of azeotropic distillation.[24] The ionomer was then redissolved in THF, and excessive zinc acetate was isolated by high-speed centrifugation. The clear solution was rotor-evaporated nearly to dryness followed by precipitation and thoroughly drying under vacuum. The carboxylation extent was determined by titration of the carboxylated PS solution in THF to a phenolphthalein end point with a solution of sodium methylate in a toluene/methanol (90:10 v/v) mixture.

BVP samples were prepared by free-radical polymerization at 60 °C under nitrogen using 0.3 wt.-% 2,2′-azoisobutyronitrile as the initiator. The copolymers were precipitated in petroleum ether and then further purified by repeating the process of dissolution in chloroform and precipitation in petroleum ether twice. The total conversion of the monomer

Table 1. Characterization data of CSEP, CSEBS and BVP.

Sample		$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Functionality mol-%
CSEP	2.8CSEP	1.30 × 10⁵	1.10 × 10⁵	1.17	2.8
CSEP	7.5CSEP	1.30 × 10⁵	1.06 × 10⁵	1.23	7.5
CSEBS	2.3CSEBS	5.62 × 10⁴	5.25 × 10⁴	1.07	2.3
CSEBS	6.8CSEBS	5.67 × 10⁴	5.25 × 10⁴	1.07	6.8
BVP	BVP4.7	5.29 × 10⁵	3.50 × 10⁵	1.51	4.7
BVP	BVP11.1	3.72 × 10⁵	2.20 × 10⁵	1.69	11.1
BVP	BVP28.9	1.95 × 10⁵	1.30 × 10⁵	1.50	28.9

was kept at less than 10%. The molar content of pyridine units in BVP were measured by nitrogen analysis.

The molecular weight and molecular weight distribution index of CSEP, CSEBS and BVP were determined by size-exclusion chromatography (SEC) with a flow rate of 1.0 mL/min, using Waters Model 510 pumps, an ERMA ERC-7512 refractive index detector and a set of columns from Polymer Standard Service, THF as the eluent, and monodispersed polystyrenes as standard samples for calibration.

The nomenclature used for ZnCSEP and ZnCSEBS samples is *x*ZnCSEP and *x*ZnCSEBS, where *x* is the carboxylation level. BVP samples are designated as BVP*y*, where *y* is the molar content of pyridine units (VP). All the characterization data of the ionomers and BVP samples are listed in Table 1.

Preparation of Blends and DSC Measurements

A ZnCSEP or ZnCSEBS solution in THF was mixed with a BVP/THF solution in the desired composition with violent agitation. Typically, 5 mL of the mixed solution was allowed to slowly evaporate in a Teflon cell with a glass cover so that the film formed in about a week. After removing most of the remaining solvent at room temperature, the sample was thoroughly dried under vacuum, first at 50 °C for 72 h and then at 120 °C for 24 h. Differential scanning calorimetry (DSC) measurements were carried out at a heating rate of 10 °C/min with a Shimadzu DSC-50 under a nitrogen atmosphere. T_g was defined as the temperature corresponding to the mid-point of heat capacity change.

Viscosity Measurements

Reduced viscosities of the solutions were measured with an Ubbelohde viscometer at 30 ± 0.1 °C. The total polymer concentration was 2.0 × 10⁻³ g/mL.

Laser Light Scattering

A modified commercial laser light scattering (LLS) spectrometer (ALV/SP-125) equipped with multi-τ digital time correlation (ALV5000) and solid-state laser (ADLAS DPY425II, output power: 400 mW at λ_0 = 532 nm) as the light source was used. The incident beam was vertically polarized with respect to the scattering plane. The refractive index increment (dn/dC) was determined using a differential refractometer.[26] Details on LLS instrumentation and theory can be found elsewhere.[27, 28] In dynamic LLS (DLS), the Laplace inversion of a measured intensity-intensity time cor-

relation function $G^{(2)}(q,t)$ in the self-beating mode can be related to a line-width distribution $G(\Gamma)$.[28, 29] In this study, inversion was done by the CONTIN program in the ALV-5000 digital time correlator. For a diffusive relaxation, Γ is normally a function of both C and q, and $(\Gamma/q^2)_{C\to0,q\to0} \to D$. $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or a hydrodynamic radius distribution $f(R_h)$ via the Stokes-Einstein equation, $R_h = (k_BT/6\pi\eta)D^{-1}$, where k_B, T and η are the Boltzmann constant, absolute temperature and solvent viscosity, respectively. All the measurements were done at $25.0 \pm 0.1\,°C$ and at a scattering angle $\theta = 15°$, and the solutions were clarified using a 0.5-µm Millipore filter.

Results and Discussion

Viscometry Studies

It is known that the reduced viscosity of a polymer pair is generally close to the weight-average values of the component viscosities, i.e., following the additivity law in case no interpolymer associations exist between the polymer chains of the components. However, positive[4, 10–14, 21, 22] or negative[4, 5] deviations from the additivity law would occur when interpolymer complexation takes place causing some changes in the hydrodynamic size of the polymer coils.

Figure 1 shows the ionomer weight fraction (F_w) dependence of 2.8ZnCSEP/BVP and 2.3ZnCSEBS/BVP blend solutions. Due to the low ion content, as expected, both series of the blend solutions show reduced viscosities close to the corresponding weight-average values
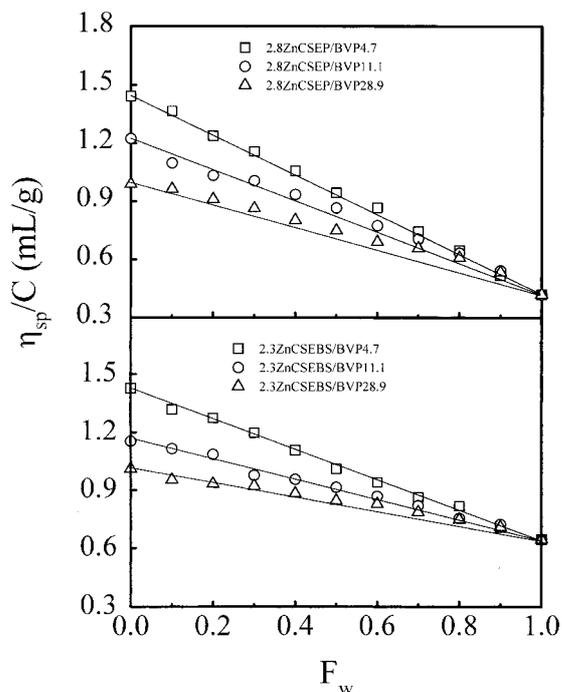

Figure 1. Reduced viscosity (η_{sp}/C) of blend solutions of 2.3ZnCSEBS/BVP (a) and 2.8ZnCSEP/BVP (b) versus blend composition.
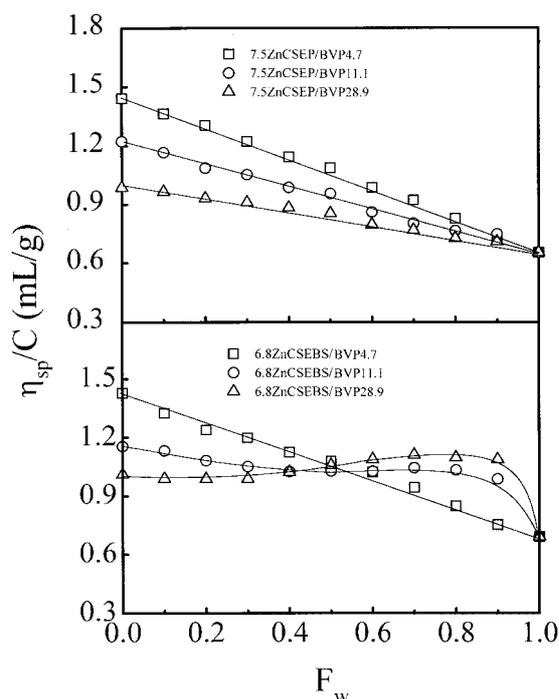

Figure 2. Reduced viscosity (η_{sp}/C) of blend solutions of 6.8ZnCSEBS/BVP (a) and 7.5ZnCSEP/BVP (b) versus the blend composition.

over the composition range. This suggests that the diblock and triblock ionomers may not form complexes with BVP having a VP content up to 28.9 wt.-%.

Figure 2 displays the reduced viscosities for the ionomeric blends with higher ion-contents, i.e., 7.5ZnCSEP/BVP and 6.8ZnCSEBS/BVP. It can be seen that even at the highest ionic level of [—COO$^-$] and VP content in the range examined, the reduced viscosities of the blends containing diblock ionomers are still almost equal to the weight-average values, suggesting that complexation probably does not occur. In contrast, the triblock ionomers exhibit different behavior, namely, the reduced viscosities follow the additivity law only when the VP content is 4.7 mol-%, while positive deviation from the additivity law was found when the VP content is higher than 11.1 mol-%. The results are highlighted in Figure 3, where η_d is defined as $\eta_d = \eta_e - \eta_a$, with η_e and η_a being the experimentally measured reduced viscosity and the value calculated from the additivity law, respectively. The molar fraction F_r of the carboxyl group (—COO$^-$) is defined as $F_r = [COO^-]/[COO^-] + [VP]$. It clearly shows that $\eta_d \approx 0$ for blends containing BVP4.7, but $\eta_d > 0$ for those comprising BVP11.1 or BVP28.9. The higher the VP content, the more pronounced the viscosity enhancement. Obviously, the marked increase in viscosity indicates the formation of interpolymer complexes between 6.8ZnCSEBS and BVP chains.

It can also be seen from Figure 3 that the curves are relatively flat, namely, the F_r values corresponding to the
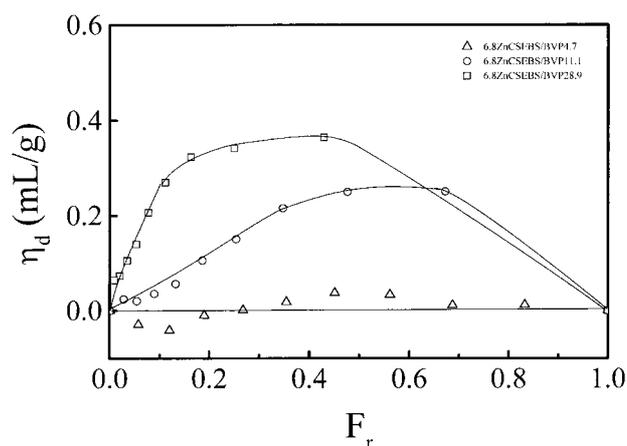
Figure 3. Reduced viscosity increment (η_d) of blend solutions of 6.8ZnCSEBS/BVP versus the molar fraction of ion groups ($F_r = [COO^-]/[COO^-] + [VP]$).
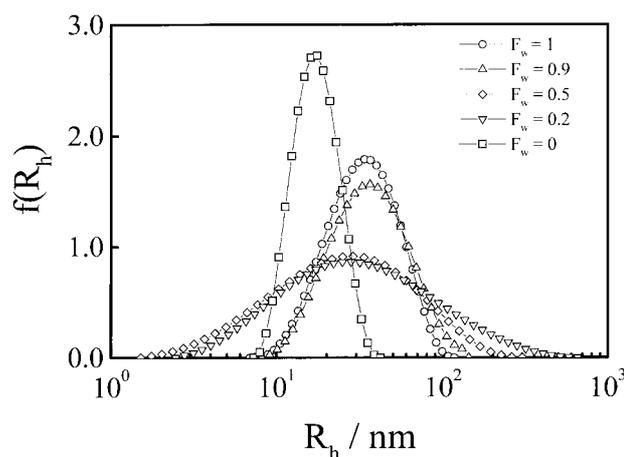

Figure 4. Hydrodynamic radius distributions $f(R_h)$ of blend solutions 7.5ZnCSEP/BVP28.9 with different compositions in THF.

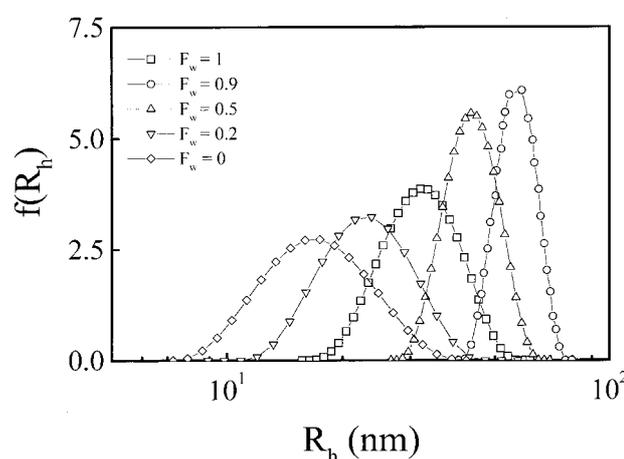
Figure 5. Hydrodynamic radius distributions $f(R_h)$ of blend solutions 6.8ZnCSEBS/BVP28.9 with different compositions in THF.

maximum viscosities are not fixed at a certain value but cover ranges of 0.5–0.7 and 0.2–0.4 for 6.8ZnCSEBS/ BVP11.1 and 6.8ZnCSEBS/BVP28.9, respectively. The literature reveals that *random* sulfonated ionomers and a VP-containing copolymer usually form stoichiometric complexes,[10–14] while the only study concerned with the complexation of *block* ionomer shows that complexes of SSEBS triblock ionomers and poly[styrene-*co*-(4-vinyl-pyridine)] have viscosity maxima in the range of $[SO_3^-]/[VP] = 1:3$ to $1:2$. There have not been enough data to generalize the rule about complexation stoichiometry.

DLS Studies

DLS proved to be a very sensitive method to investigate the aggregation of ionomers[4, 31–34] and the complexation between unlike polymers,[5, 21, 22] since aggregation and complexation are accompanied by a change in hydrodynamic radius. In previous work,[5, 21, 22] we reported that interpolymer complexation due to both H-bonding and ionic interaction usually gave rise to a larger hydrodynamic radius with a narrowing hydrodynamic radius distribution. Note that the complexes due to H-bonding are in fact intermacromolecular aggregates, which are not stable in solution and often precipitate causing some difficulties in monitoring the complexation.[5] However, ionic interaction complexes are usually soluble[21, 22] and can be readily examined by means of DLS. Especially, in the case of a complex comprising a block ionomer in which only one kind of block forms the complex, but the others remain soluble, stable complex solutions can be expected.

Figure 4 shows the hydrodynamic radius distributions $f(R_h)$ of 7.5ZnCSEP/BVP28.9 in THF with different compositions compared to those of the component polymers. It can be seen that the distribution of pure 7.5ZnCSEP ($F_w = 0$) seems rather broad for a monodispersed iono-

mer. This is caused by the interchain association of the ionomers due to the aggregation of the ionic groups in the non-polar solvent THF.[31–35] Blend solutions show even broader distributions covering the whole size range of the two components with a peak between them. This fact further corroborates the viscometry results, namely, that for the diblock ionomer blends, 7.5ZnCSEP/BVP28.9, no significant intercomponent complexation takes place. It is noteworthy that the curves for the cases $F_w = 0.2$ and 0.5 show very broad distributions extending to the regions of very low and high R_h. As the R_h distribution curves were obtained from the Contin program, the wider the distribution, the more enhanced is the effect of noise on the results. Thus, the contributions from the very low and high R_h part were probably overdrawn.

Figure 5 is a typical plot of the hydrodynamic radius distribution $f(R_h)$ of triblock ionomer blend solutions, i.e., 6.8ZnCSEBS/BVP28.9 in THF. Like ZnCSEP, ZnCSEBS also has a relatively wide distribution due to

the association of its chains. However, the blend solutions display a behavior, which is completely different from the diblock ionomer blends. Compared to the pure components, the distribution curves of the blends are shifted to a much higher size range depending on the blend composition. As the weight fraction of ZnCSEBS increases, R_h increases with narrowing $f(R_h)$, indicating that the component polymer chains in solution are no longer independent but form some intermolecular complex particles as a result of the coordination between the VP groups in BVP and zinc ions in the ionomers.

A comparison between the average hydrodynamic radii ($\langle R_h \rangle$) of the two series of blend solutions as a function of blend composition is also made. Blend solutions comprising the diblock ionomer exhibit $\langle R_h \rangle$ following the weight-average additivity law within experimental error, which further indicates that ZnCSEP can not form detectable complexes with BVP. However, the triblock ionomer blends behave differently. For the case of higher metal ion content, i.e., 6.8ZnCSEBS/BVP28.9, $\langle R_h \rangle$ significantly increases above the additivity and reaches a maximum as the triblock ionomer dominates ($F_w \approx 0.9$). Maximum $\langle R_h \rangle$ reaches 55 nm, which is about twice the corresponding weight-average value. Even in the case of 2.3ZnCSEBS with low ion-content, an increase in $\langle R_h \rangle$ is detected indicating that the component polymers also form complexes to some extent. It is worth noting that no complexation in 2.3ZnCSEBS/BVP28.9 blends could be evidenced by means of viscometry. This is understandable since DLS is more sensitive toward larger particles than viscometry.

Complexation in Bulk

When polymer chains form complexes, some changes take place in their segmental mobility resulting in variances in T_g.[5, 10, 21, 22] Figure 6 is a typical plot of DSC curves for the blends of 6.8ZnCSEBS/BVP28.9. It can be seen that the 6.8ZnCSEBS triblock ionomer has two T_gs, i.e., one at −41 °C associated with EB blocks, and the other one at 88 °C with ionomeric PS blocks. Compared with the corresponding T_gs of SEBS, i.e., −41 °C and 80 °C for EB and PS blocks, respectively,[22] the T_g of ionomeric PS blocks ($T_{g,PS}$) increases as a consequence of ionic aggregation, while the T_g of non-ionic EB blocks is almost constant. In the blends of 6.8ZnCSEBS/BVP, the T_g of EB is also not affected. This is understandable as complexation only occurs in the domains of ionomeric PS, however, T_g of the hard phase is markedly improved through blending.

With increasing F_w from 0.4 to 0.9, T_g increases from 91 to 102 °C, which evidences that 6.8ZnCSEBS and BVP chains undergo complex formation. Similar results were observed for complexes formed by *sulfonated* SEBS triblock ionomers with copolymers containing pyridine
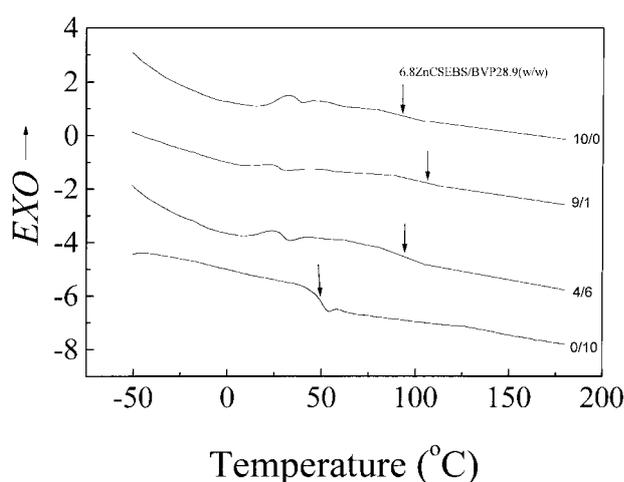

Figure 6. DSC curves of 6.8ZnCSEBS and BVP28.9 and their blends at different compositions (indicated in the figure).

units.[22] In contrast, the T_gs of both non-ionic EP and ionomeric PS blocks of 7.5ZnCSEP (−59 °C and 92 °C, respectively) are slightly affected by blending with BVP. The invariance in T_g of PS microdomains suggest that even at the highest level of ionic interactions in the range examined, diblock ionomer ZnCSEP can not form complexes with BVP chains in bulk. This is consistent with the conclusion drawn from the solution behavior.

The Role of Chain Architecture in Complexation

It is known that the driving force of the complexation in the present systems is the coordination between Zn ions and the pyridine ligand.[36] However, triblock ionomer ZnCSEBS and diblock ionomer ZnCSEP with a similar content in ionomer block, the same type of ionic groups and a close ionic level exhibit very different complexation behavior with BVP. Although the marked architectural effect of the block ionomers on complexation has not been fully understood yet, we would like to interpret it in terms of the difference in structural characters of the two types of the ionomers. It is well known that in a nonpolar solvent such as THF and in bulk, the ionic groups of an ionomer often aggregate into multiplets or clusters.[31−35] For block ionomers, such an aggregation certainly promotes micellization or phase separation between ionomer and neutral block. However, diblock and triblock may cause very different micelle structures. As shown in the schematic presentation in Scheme 1, the PS microdomains of triblock ionomer ZnCSEBS are connected by EB chains so that every triblock ionomer associate contains several such microdomains while that of diblock ZnCSEP contains only one. This model could be supported by of viscosity and hydrodynamic radius data as follows. Although the molecular weight of SEP (1.18×10^5) is substantially higher than that of SEBS (5.25×10^4), the corresponding Zn ionomers present very
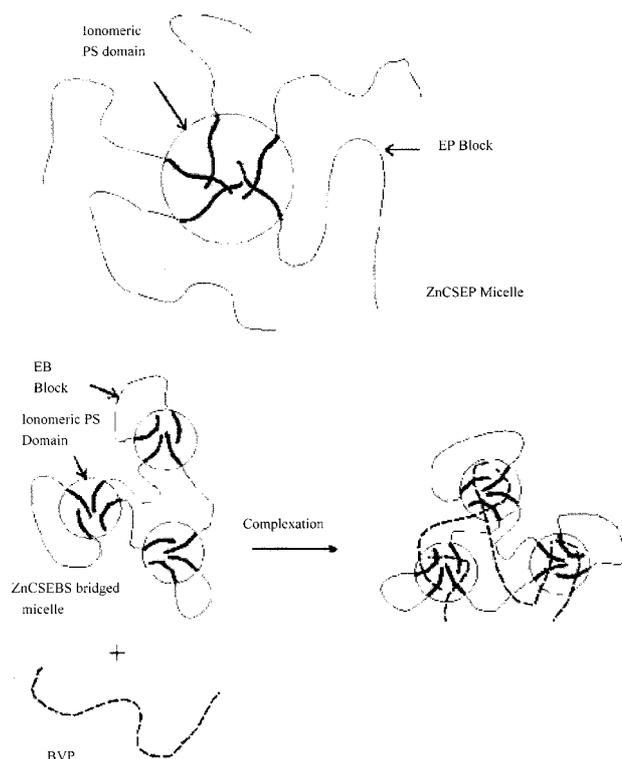
Scheme 1. A schematic plot of the complexation of diblock ionomer ZnCSEP and triblock ionomer ZnCSEBS with BVP.

similar reduced viscosities, i.e., around 1–1.5 mL/g (Figure 2), and similar average hydrodynamic radii around 30 nm. According to this model, the average distance between neighboring PS microdomains of ZnCSEBS, which is restricted by the EB chain length ($\overline{M}_n$ = 3.3×10^4), is obviously much less than that in ZnCSEP. When BVP was mixed with the triblock ionomer in solution, VP groups along a long enough BVP chain ($\overline{M}_w$ = 5.3×10^5) are able to interact with the ionic groups of ZnSEBS simultaneously existing in different microdomains. This process of interpolymer complexation of course leads to a pronounced increase in both viscosity and average hydrodynamic radius. In contrast, in the case of BVP and diblock ZnCSEP, the VP groups of a BVP chain actually can interact with the ionic groups in one microdomain only due to the long distance between the PS microdomains in solution. Besides, a BVP chain can be incorporated into a microdomain partially only; otherwise, it causes a substantially unfavorable conformation entropy. Therefore, only a small portion of the VP groups is able to interact with the ionic groups. It is generally accepted that cooperative interaction plays a critical role in polymer complexation, namely, a minimum interacting chain length or amount of interacting segments is needed for complex formation.[4, 5] Obviously, the blend solutions of BVP and triblock ionomers meet this requirement, but diblock ionomers do not.

It is worth noting that this argument does not exclude the possibility of the complex formation of diblock ionomers provided the interaction is strong enough. In fact, as we reported previously, the Zn diblock ionomer of *sulfonated* SEP and BVP do form interpolymer complexes as evidenced by viscosity and LLS measurement.[25] This obvious disparity between sulfates and carboxylate ionomers can be understood in terms of the marked difference in ionic interaction between the two kinds of ionomers.[14, 37]

Conclusions

The complexation behavior of diblock ionomer ZnCSEP or triblock ionomer ZnCSEBS with BVP has been investigated by means of viscosity measurement, DLS and DSC both in solution and in bulk. It is found that triblock ionomeric ZnCSEBS can form complexes with BVP, exhibiting enhanced viscosity, increasing hydrodynamic radius with narrowing hydrodynamic radius distributions in solution, and an increased T_g of the ionomeric PS blocks in bulk, while ZnCSEP can not The difference in their chain architectures leading to different micelle-like structures is thought to be responsible for the different complexation behavior.

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