

# Interpolymer complexes comprising block copolymers due to specific interactions

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## Abstract

Two kinds of supramolecular assembly, i.e., macromolecular complex comprising block copolymers were investigated by viscometry and static and dynamic light scattering. In the blend solutions of poly(styrene-*co*-methyl methacrylate) (PS-*b*-PMMA) and hydroxyl-containing modified polystyrene (PS(OH)), the hydrogen bonding between the PMMA block and PS(OH) leads to the complex formation. In the solutions of Zn sulfonated poly(styrene-*b*-ethylene-*co*-propylene) (ZnSSEP) and poly(butyl methacrylate-*co*-vinyl pyridine) (BVP), the ligand–metal coordination between BVP and the polystyrene ionomer block causes complexation. Both kinds of complexation induce nano-size, soluble complexes with micelle-like structure, which is stabilized in the solutions by the soluble, non-complexed blocks. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Hydrogen bonding; Ionic interaction; Complexation

## 1. Introduction

Macromolecular complexes are interpolymer associates of two unlike polymers bound together by secondary binding forces. Among these forces, hydrogen-bonding and ionic interactions have received most attention in the literature.[1,2] It was observed that mixing solutions of a proton-donating polymer and a proton-accepting polymer or an anionic polymer and a cationic polymer always lead to complex formation as precipitate. Precipitation causes difficulties in examining the complexation process and characterizing the structure of the complex aggregate. In the traditional complexation studies, every segment of each component often has a specific interaction group.

In recent years, in our laboratories, attention has been focused on the dependences of the complex formation on intensity and density of the interactions. A systematic study for the systems in which the density of intercomponent hydrogen bonding is adjustable has been carried out in our laboratories [2]. By using a combination of techniques including dynamic and static light scattering, fluo-

roscopy and viscometry for solutions of a series of polymer pairs, the transition from separated coils to complex aggregates has been found as the intermolecular hydrogen bonding is strengthened [3–10].

On the other hand, ion–ion interactions or ligand–metal coordination leading to aggregations of polymer chains have been studied for various ionomer-containing polymer pairs, e.g., sulfonated ethylene–propylene terpolymer/poly(styrene-*co*-4-vinyl pyridine) (STVPy) [11], and sulfonated polystyrene/poly(ethyl acrylate-*co*-4-vinyl pyridine) [12], etc. In the systems with the ion-related interactions, polymer–polymer aggregations are often accompanied by microgel formation or gelation. This hinders clear understanding the process of aggregation or complexation between the component polymers in solutions by means of routine characterization methods.

Differing from the ordinary polyelectrolyte complexes, mixing a block copolymer containing a polyelectrolyte block with an oppositely charged polyelectrolyte in solution may form soluble complexes [13–16]. For example, poly(ethylene oxide-*b*-methacrylate) anions and poly(*N*-ethyl-4-vinyl pyridinium) cations [15] form water-soluble stoichiometric complex due to the attraction forces between the opposite charges. The presence of the soluble poly(ethylene oxide) blocks renders the solubility of the complex. Quite recently, soluble complex composed of

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poly(ethylene glycol)-*b*-poly(aspartic acid) copolymer and lysozyme was reported [16].

In this communication, we extend our long-term research on interpolymer complex to the systems comprising diblock copolymer AB. In such AB/C blend solutions, block A of the diblock copolymer has either hydrogen or ligand–metal coordination interactions with homopolymer (or random copolymer) C. Due to the interactions, A and C may form some kind of molecular complexes. Besides, precipitation or gelation can be prevented due to the presence of the solubilizing block B.

## 2. Experimental

Diblock copolymer ZnSSEP, i.e., Zinc salt of sulfonated poly(styrene-*b*-ethylene-*co*-propylene) (SEP) was prepared by successive sulfonation and neutralization of commercial product of SEP (Shell). The characterization data of SEP: PS 29 wt.%, weight-average molecular weight  $1.30 \times 10^5$  and  $M_w/M_n$  1.09; in ZnSSEP, sulfonation degree 7.5 mol% based on PS block.

Diblock copolymer poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) was prepared by anionic polymerization. The molecular weight of polystyrene block and poly(methyl methacrylate) block are  $3.74 \times 10^4$  and  $2.4 \times 10^4$ , respectively.  $M_w/M_n$  is 1.20.

Poly(*n*-butyl methacrylate-*co*-4-vinyl pyridine) (BVP) was prepared by free radical polymerization, with 29 wt.% content of pyridine-containing units and molecular weight  $2.23 \times 10^5$ .

PS(OH), copolymer of styrene and hydroxyl-containing monomer *p*-(hexafluoro-2-hydroxyisopropyl)- $\alpha$ -methyl styrene (HFMS) was prepared by free radical polymerization [17]. The HFMS content was 20 mol% and the molecular weight  $M_n$  and  $M_w/M_n$  were found to be  $2.18 \times 10^4$  and 1.44 by SEC, respectively.

The experimental details for the measurements of size exclusion chromatography, viscometry and static and dynamic light scattering were reported in our previous publications [5–8].

## 3. Results and discussion

### 3.1. Complexation between ZnSSEP and BVP

The coordination complexation between pyridine unit and metal ions was investigated in both solutions and bulk for many polymer blends,[18–22] but not for diblock copolymer-containing blends. Fig. 1 shows distributions of hydrodynamic radius of ZnSSEP, BVP and their blends of different compositions in THF. The BVP solution shows a relatively broad distribution with average  $\langle R_h \rangle$  of 17 nm. The ionomer solution of ZnSSEP presents a very broad distribution of  $R_h$  ranging from 10 to 100 nm with average

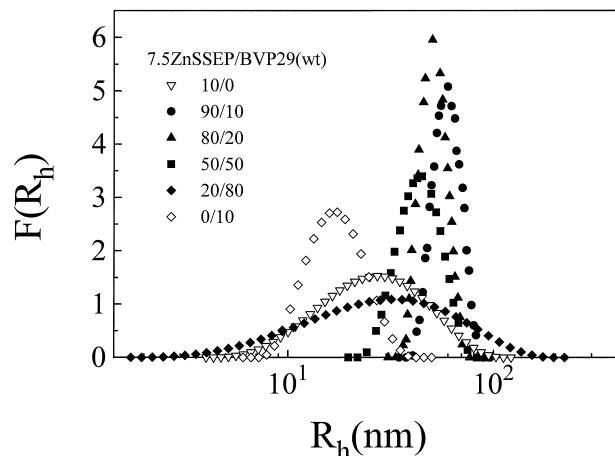


Fig. 1. Hydrodynamic radius distributions of ZnSSEP, BVP and their blends in THF.

$\langle R_h \rangle$  about 31 nm. This indicates that in THF, ZnSSEP may form intermolecular associate due to the interactions between the solvated ionic pairs. A quantitative estimation of the association is given by the static light scattering measurements, i.e., the apparent molecular weight of ZnSSEP and molecular weight of the parent resin SEP are  $2.37 \times 10^6$  and  $1.3 \times 10^5$ , respectively. So the ratio of the former to the latter, namely the aggregation number of the associates is found to be 18.

For the blend solutions with compositions of ZnSSEP/BVP 9/1, 8/2 and 1/1 w/w, the peaks associated to the single components disappeared while new peaks at around a few tens of nanometers were observed. These much narrower distributions with high  $\langle R_h \rangle$  can undoubtedly be attributed to the complex particles composed of the block copolymer and BVP. The solutions containing these dispersed nano-particles are transparent and very stable on long standing without gelation and precipitation. It implies that the poly(ethylene-*co*-propylene) blocks, which are still dissolved in THF, are probably located at the shell of the particle stabilizing the particles in the solutions.

The blend solution with low content of the ionomer, i.e., ZnSSEP/BVP 2/8 shows a rather broad distribution largely overlapping those of the single components. It indicates the coexistence of both single molecules of ZnSSEP and BVP and their complex aggregates.

Fig. 2 shows average  $\langle R_h \rangle$  and reduced viscosity of the blend solutions as functions of blend composition. Both show considerable positive deviation from the additivity law. This is a clear evidence of interpolymer aggregation. Two curves present similar trends with a maximum at around a weight ratio of ZnSSEP/BVP 90/10, i.e., interaction site ratio ( $[\text{SO}_3^-]/[\text{VP}]$ ) at around 1/1. The maximum  $\langle R_h \rangle$  of the blends reaches 53 nm which means that the average volume of the complex aggregate is 5 and 30 times as large as the ZnSSEP associate and BVP coils, respectively.

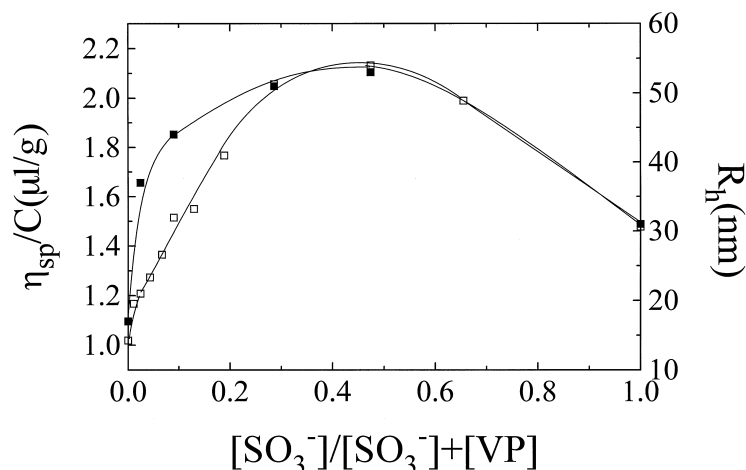


Fig. 2. Reduced viscosity and average hydrodynamic radius of the blend solutions of ZnSSEP and BVP as functions of the  $[\text{SO}_3^-]$  fraction ( $[\text{SO}_3^-]/[\text{SO}_3^-] + [\text{VP}]$ ). Solid square and open square refer to the average hydrodynamic radius and reduced viscosity, respectively.

### 3.2. Complexation between PS-*b*-PMMA and PS(OH)

The micellization of block copolymers in a *selective solvent* which is a good solvent for a block but precipitant for the other has been extensively studied [23]. Here we report the formation of micelle-like structure of block copolymer PS-*b*-PMMA with PS(OH) in a *non-selective solvent* induced by complexation between PS(OH) and PMMA blocks.

In this research group, great efforts have been made in exploring complexation of modified PS, i.e., PS(OH) containing strong proton-donating group of  $(\text{CF}_3)_2(\text{OH})\text{C}-$ , with various poly(alkyl acrylate)s [3–10]. It was found that mixing toluene solutions of PMMA and PS(OH) with a certain level of OH content caused complexation as evidenced by the appearance of large aggregates in LLS measurements. Usually, such aggregates are not stable and easy to precipitate on standing. A common feature of such blend systems is that the reduced viscosity of the blend solutions show a substantial negative deviation from the additivity law, which implies that the polymer chains collapse in the process of complexation.

Typical light scattering results for PS-*b*-PMMA and PS(OH) and their blend (1/1 w/w) in toluene are shown in Fig. 3. Both PS(OH) and the block copolymer show broad distributions with peaks located at 3 nm and 6.5 nm, respectively. A remarkable change occurs when the two solutions are mixed, i.e., both the peaks associated with the components disappear and a new one emerges at much larger  $R_h$  value around 84 nm. Based on our results on complexation between PS(OH) in PMMA, it is reasonable to think that in the present case, the complexation between PS(OH) and PMMA block causes the chain collapse and consequent aggregation. However, due to the presence of the soluble PS blocks in toluene, no precipitation takes place. The PS chains surrounding the complex core prevent the particles from further aggregation.

Similar results were obtained for the solutions containing PS-*b*-PMMA and PS(OH) with different (8, 30, 50 mol%) hydroxyl contents. In all the cases studied, mixing the solutions led to stable, transparent dispersions of the micelle-like particles with size in the range of 70–100 nm depending on the hydroxyl content in PS(OH). The larger the content, the larger the aggregation number but the smaller the size. This means that strengthening the interactions leads to a more compact core composed the highly collapsed chains.

Based on the results above, a schematic representation for the complexation between PS(OH) and PS-*b*-PMMA is proposed as shown in Fig. 4.

### 3.3. A comparison between two kinds of complexation

The two kinds of complexation discussed above have some similarities, namely, the specific interactions exist only between the random copolymer and one type of block of the block copolymers. Both form complex particles

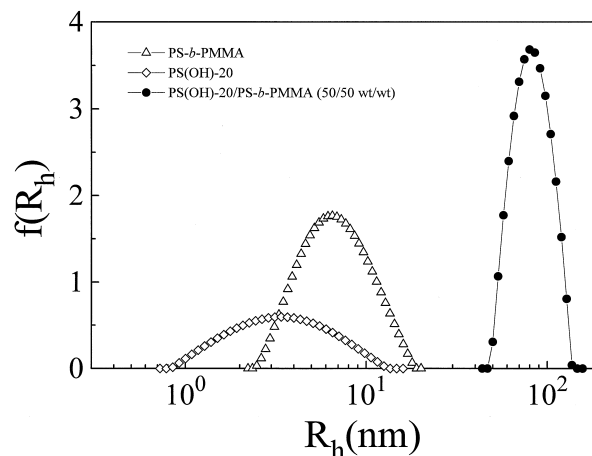


Fig. 3. Hydrodynamic radius distributions of PS(OH), PS-*b*-PMMA and their blends in toluene.

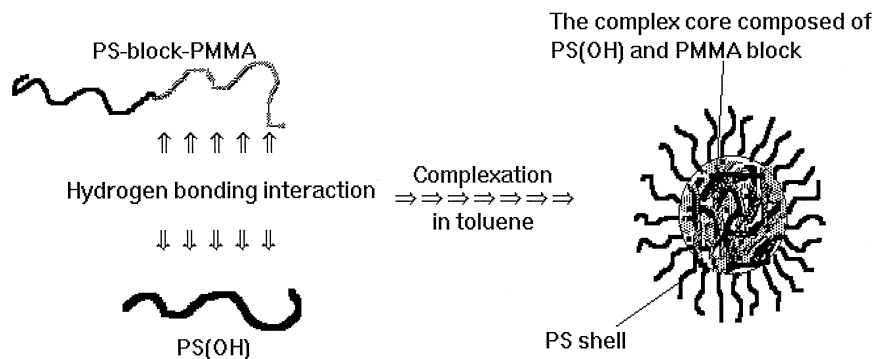


Fig. 4. A schematic illustration of the formation of complexes between PS-*b*-PMMA and PS(OH).

stably dispersed in solutions with size ranging from a few tens to one hundred nanometers. On the other hand, the two kinds of complexation have distinct differences in their internal structure of the complex aggregates.

In our long-term studies on polymer–polymer complexation, it was found that compared to the additivity law, the complexation due to hydrogen-bonding as in PS(OH) and PMMA always causes a dramatic viscosity decrease while the complexation comprising ionomers leads to a viscosity increase. We discussed this difference in our previous work [20]. The viscosity decrease was attributed to a relatively “tight” chain-to-chain structure which accompanies coil collapse while the viscosity increase to a loose, crosslink-like structure, which can be highly swollen by solvent. This difference maintains in current complexations comprising block copolymers. As shown in Fig. 2, the reduced viscosity of ZnSSEP and BVP shows a considerable increment over the whole composition range and reaches its maximum being about 1.5 times of the additivity value. This implies that in the complex aggregates, although the sulfonated polystyrene blocks and BVP chains are linked together by the ligand–Zn coordination, the two kinds of chain are still sufficiently swollen. In contrast, in the case of PS-*b*-PMMA and PS(OH), the reduced viscosity shows a negative deviation from the additivity law over the whole composition range, which will be reported in detail in our forthcoming paper. This is an indication that the hydrogen bonding causes a segment-pairing structure leading to rather compact cores of the dispersed particles.

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