ELSEVIER

Polymer 42 (2001) 151–159

polymer

www.elsevier.nl/locate/polymer

Intermacromolecular complexation because of specific interactions 11. Ionic interaction complexation and its comparison with hydrogen-bonding complexation

Guangzhao Zhang[a], Ming Jiang[a,*], Lei Zhu[a], Chi Wu[b,c]

[a]Institute of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China
[b]Chemistry Department, The Chinese University of Hong Kong, Shatin, Hong Kong, People's Republic of China
[c]The Open Laboratory of Bond-Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, People's Republic of China

Received 19 October 1999; received in revised form 4 April 2000; accepted 24 April 2000

Abstract

The ionic interaction complexation between metal carboxylated polystyrene ionomers and poly(butyl methacrylate-*co*-vinyl pyridine) (BVP) in both solution and bulk was studied by viscometry, laser light scattering (LLS) and differential scanning calorimetry (DSC) and compared with that between BVP and carboxylated polystyrene (CPS), in which the interacting groups are in acid form. The results show that both kinds of complexation strongly depend on the level of the specific interaction and give rise to an increased hydrodynamic radius over the component polymer coils. However, the ionic interaction complexation generally results in an increased viscosity in the solution and almost always exhibits two glass transition temperatures (T_gs), in contrast, the hydrogen bonding complexation leads to a decreased viscosity and only one T_g. The different behavior is attributed to the difference in spatial distributions of the interacting sites in the complexes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Intermolecular complex; Specific interactions; Ionomer

1. Introduction

Intermacromolecular complexation between unlike chains through secondary bonding or specific interactions has aroused considerable interests experimentally and theoretically for years [1–21], because of its significant importance in understanding some biological processes and self-assembly of molecules, as well as in developing new functional assembled materials. The development made on H-bonding complexation in the last decade has been reviewed quite recently by Jiang et al. [1]. It has been demonstrated that H-bonding complexation in solution generally shows a decreased viscosity compared to the expected value by additivity law and only one T_g in bulk. By laser light scattering (LLS), we found that H-bonding complexation usually leads to an increase in hydrodynamic radius and narrowing in hydrodynamic radius distribution compared to the component polymer coils in solution [1–4]. On the other hand, in the literature, attention has also been paid to the intermacromolecular complexation caused by the ionic interaction [4]. The complexation of sulfonated random ionomers such as those based on poly(ethylene-*co*-propylene-*co*-ethylidiene nobornene) (SEPDM) [6–8] and poly(phenylene oxide) (SPPO) [9,10] and polystyrene (SPS) [9–11] with pyridine-containing random copolymer, i.e. poly(styrene-*co*-4-vinylpyridine) (SVP) in nonpolar and polar solvents were investigated by viscometry in several laboratories [6–11]. MacKnight et al. [12] assessed the complexation between SPS and poly(ethyl acrylate-*co*-4-vinylpyridine) (EVP) in solution by means of the fluorescent probe technique. These studies reported that the ionic intercomponent complexation in bulk often show two glass transition temperatures (T_gs) in bulk, and an increase in viscosity in solution. Similar behavior has been observed for the blends containing ionic interaction groups located at the chain ends exclusively leading to non-covalent block or graft architectures [13–19]. Our investigations on the blends of triblock ionomers based on poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) and pyridine-unit-containing

---

* Corresponding author. Tel.: +86-21-6564-3919; fax: +86-21-6564-0293.
E-mail address: mjiang@fudan.edu.cn (M. Jiang).

0032-3861/01/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00332-3

Table 1
Characterization data of precursors of CPS ionomers and BVP

Sample	M_w	M_n	M_w/M_n	Carboxylation extent (mol%)
1.2CPS	1.54 × 105	1.43 × 105	1.08	1.2
7.2CPS	1.54 × 105	1.43 × 105	1.08	7.2
BVP4.7	5.29 × 105	3.5 × 105	1.51	4.7
BVP11.1	3.72 × 105	2.2 × 105	1.69	11.1
BVP28.9	1.95 × 105	1.3 × 105	1.5	28.9

copolymers indicate the complexation between the block ionomer and the copolymer leading to complex aggregates [20,21].

The difference between the two kinds of complexation has puzzled us for a long time. As both the ionic-interaction complexation and H-bonding complexation are dependent on many factors such as the molecular weight and its distribution of the component polymers, the level of the interaction, the solvent used, making a comparison by using two polymer blends differing only in the type of the specific interactions is not easy. Fortunately, we accumulated some data on complexation between the carboxylated polystyrene (CPS) and pyridine-containing copolymers because of H-bonding [2,3]. Parallel to the previous work, in this article, we report the complexation between CPS ionomers and BVP, due to ionic interactions. The blend systems used in the two studies are similar in chemistry. The main difference is that the interacting sites in CPS are carboxylic acid and in the ionomers the corresponding metal ions. Based on the results of the two systems, we attempt to explore the origin of the difference and correlate it with the complex structure.

2. Experimental

2.1. Materials

All polystyrene samples were prepared by anionic polymerization in cyclohexane initiated by butylithium (*n*-BuLi) at 50°C. CPS samples with different carboxylation extent were synthesized by partially carboxylating the polystyrene via a mild Friedel–Crafts acetylation and a subsequent haloform oxidation of the resulting acetyl groups with cetyltrimethylammonium bromide as the phase transfer catalyst [22]. The lithium and zinc salts of CPS were prepared by neutralizing CPS in THF with lithium methylate and zinc acetate in toluene/methanol (90/10 v/v) mixture, respectively. The carboxylation extent was determined by titration of the CPS solution in THF to a phenolphthalein end point with a solution of sodium methylate in toluene/methanol (90/10 v/v) mixture.

BVP samples were prepared by free radical polymerization of butyl acrylate and 4-vinyl pyridine at 60°C under nitrogen using 0.3 wt% azobiisobutyronitrile as the initiator. The copolymers were precipitated in petroleum ether and then further purified by repeating the process of redissolution in chloroform and reprecipitation in petroleum ether twice. The total conversion of the monomer was kept at less than 10%. The molar contents of pyridine units in BVP were measured by nitrogen analysis.

The molecular weight and molecular weight distribution index of CPS and BVP were determined by size-exclusion chromatography (SEC) with a flow rate of 1.0 ml/min, using a Waters Model 510 pump, an ERMA ERC-7512 refractive index detector and a set of columns from Polymer Standard Service and monodispersed polystyrenes for calibration.

The nomenclature used for the CPS ionomer is *x*-MCPS, where *x* is the carboxylation degree in mole percent, and M designates the counterion, either Li or Zn. BVP samples are designated as BVP-*z*, where *z* is the mole content of pyridine unit. All the characterization data of the ionomer and BVP samples used for the studies on intermacromolecular complexation are listed in Table 1.

2.2. Viscosity measurements

Reduced solution viscosity measurements were made with an Ubbelodhe viscometer at 30 ^ 0.1°C with a total polymer concentration of 2.0×10^{-3} g/ml.

2.3. Laser light scattering

A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlation (ALV5000) and a solid-state laser(ADLAS DPY425II, output power = 400 mW at $\lambda_0 = 532$ nm) as light source was used. The incident beam was vertically polarized with respect to the scattering plane.

In dynamic LLS, i.e. DLS, the line-width distribution $G(\Gamma)$ can be calculated from the Laplace inversion of the intensity–intensity time correlation function $G^{(2)}(t,q)$ [23]. In this study, the inversion was carried out by the CONTIN programme supplied with the ALV-5000 digital time correlator. For a diffusive relaxation, Γ is normally a function of both C and q, at $C \to 0$ and $q \to 0$, $\Gamma/q^2 \to D$. Therefore, we can transfer $G(\Gamma)$ obtained in a finite concentration and at a certain scattering angle into a translational diffusion coefficient distribution $G(D)$. Further, $G(D)$ can be converted into a hydrodynamic radius distribution $f(R_h)$ by using the Stokes–Einstein equation, $R_h = (k_B T/6\pi\eta)D^{-1}$, where k_B, T and η are the Boltzmann

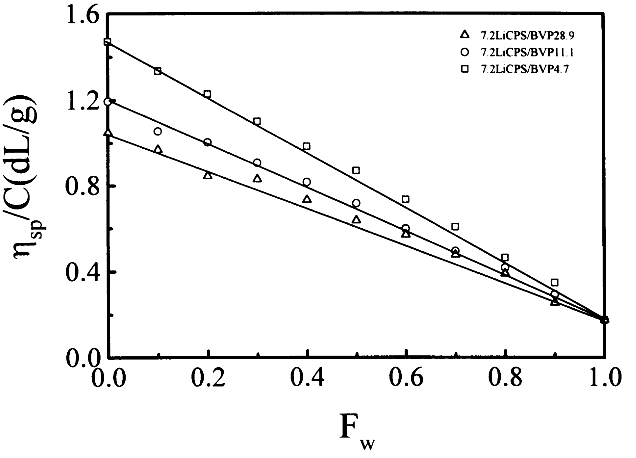


Fig. 1. Reduced viscosity of blend solutions of 7.2LiCPS/BVP versus the blend composition (7.2LiCPS content in wt%).

constant, the absolute temperature and the solvent viscosity, respectively.

All DLS measurements were performed at $\theta = 15°$ and 25 ^ 0.1°C, and all samples with a total polymer concentration of 1.0×10^{-4} g/ml were clarified using a 0.5-μm Millipore filter.

2.4. DSC measurements

THF solutions of an ionomer and BVP were mixed 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. The blend 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. DSC measurements were carried out with a Shimadzu DSC-50 at a heating rate of 10°C/min under nitrogen atmosphere. T_g was defined as the temperature corresponding to the midpoint of heat capacity change.

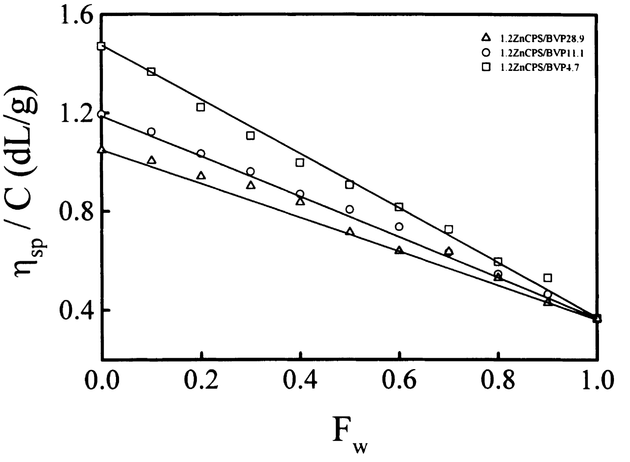


Fig. 2. Reduced viscosity of blend solutions of 1.2ZnCPS/BVP versus the blend composition.

3. Results and discussion

3.1. Complexation in solution studied by viscometry

Viscometry is a simple and effective technique for monitoring complexation of polymer blend solutions. Generally, if no specific interactions exist in the polymer pair, the component polymer coils spatially isolate from each other in dilute solutions, and the reduced viscosity of the polymer pair is close to the additivity law of the component viscosity. However, positive [4,6–11,20,21] or negative [1–4] deviations from the additivity law may occur if the specific interactions between the polymer pair are strong enough, suggesting intermacromolecular complexation.

Fig. 1 shows the reduced viscosities of the LiCPS/BVP blend solutions versus the weight fraction of the ionomer LiCPS (F_w). It shows that even when both LiCPS and BVP have the highest content of functional groups in the range we examined, the reduced viscosity of the blend solution follows the additivity law of the component viscosity. This means there are no significant interactions between the –COOLi and VP units. In other words, the alkali metal salt of CPS, i.e. LiCPS chains cannot form intermacromolecular complexation with BVP. Figs. 2 and 3A show the blend viscosity behavior of the transition metal salt ZnCPS and BVP. In Fig. 2 the reduced viscosities of the blend solutions of 1.2ZnCPS and BVP with different VP contents are almost equal to the weight average values, indicating that the content of –COOZn here is too low to form complexes. However, when the carboxylation extent is increased to 7.2 mol%, the results are different as shown in Fig. 3A. Although the reduced viscosities of 7.2ZnCPS/BVP4.7 still follow the additivity law as the VP content is only 4.7 mol%, the blends show positive deviation as VP content reaches 11.1 and 28.9 mol%. This dependence of the viscosity on the VP content in BVP can be shown more clearly in the plot of η_d against F_r, where η_d is the difference between the experimentally measured reduced viscosity η_{sp}/C and the corresponding value calculated from the additivity law, and F_r is the mole fraction of [–COO$^-$], i.e. $F_r =$ [–COO$^-$]/[–COO$^-$] + [VP] (Fig. 4). It clearly shows that $\eta_d \cong 0$ for the blends containing BVP4.7 over the whole composition range; but $\eta_d > 0$, for those with BVP11.1 and BVP28.9. Moreover, the higher the VP content, the larger the viscosity enhancement. The marked increase in viscosity indicates the formation of the intermacromolecular complexes between 7.2ZnCPS and BVP chains.

It has been found that ionic interaction complexation in solution depends on the counterion and solvent [7–11,20,21], especially the polarity of the solvent has a strong influence on the complexation of ionomeric blends when an alkali or alkaline earth metal served as the counterions [7–11,20,21]. Lundberg et al. [7] reported that the alkali or the alkaline earth metal neutralized SEPDM hardly form complexes with SVP in nonpolar solvent. Feng et al. [8] found that the complexation occurred in such ionomeric

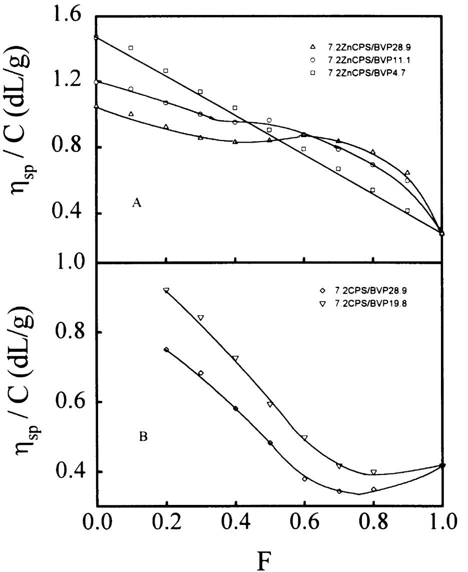


Fig. 3. Reduced viscosity of blend solutions of 7.2ZnCPS/BVP (A) and 7.2CPS/BVP (B) versus the blend composition.

blends when a minor polar solvent was added to the blend solutions. Pan et al. [9,10] also found that the minor polar cosolvent plays an important role in the formation of complexes between the alkali salts SPS and SVP in the nonpolar solvent chloroform. Weiss et al. [11] reported that both the alkali and alkaline earth metal salts of SPS can form complexation with SVP in the polar solvent *N*,*N*-dimethylformide (DMF). We previously reported [20,21] that alkali and alkaline earth metal salts of sulfonated SEBS triblock ionomers form complexes in the low polarity solvent THF, which may act as an alternative of a mixture of a nonpolar solvent and a little polar solvent. All the above facts suggest that the formation of the complexation depends on the solvating ability of the solvent to the ionic groups. In the present work, we think that the poor solvation of THF on lithium because of the relatively weak acidity of carboxyl and the inability of the coordination of pyridine to lithium ion are responsible for the absence of complexation between LiCPS and BVP.

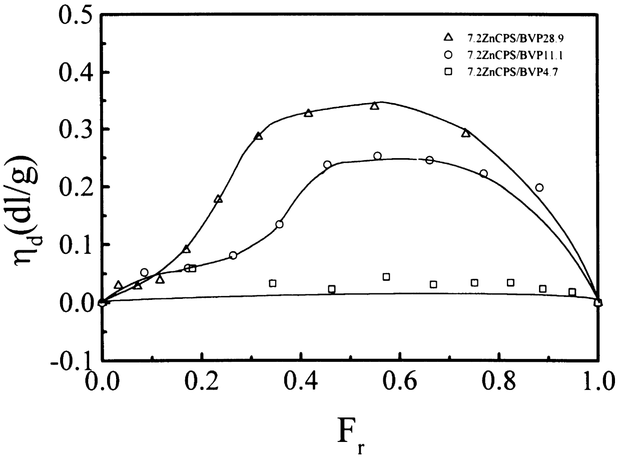


Fig. 4. Reduced viscosity increment (η_d) of blend solutions of 7.2ZnCPS/BVP versus the molar fraction of ion groups (F_r = [COO$^-$]/[COO$^-$] + [VP]).

Unlike alkali and alkaline earth metal salts, transition metal salts of sulfonated ionomers can form complexes with pyridine unit containing copolymers in either polar or nonpolar solvents [7–11,20,21]. It is generally accepted that the intermacromolecular complexation is because of the ligand–metal coordination between the transition metal ions and VP groups, independent of the solvation of the cations. Following this point of view, it is understandable that ZnCPS forms complexes with BVP in THF, provided the content of ionic groups reaches a certain value.

The viscosity behavior of ionic inteaction complexation is very differnt from that of H-bonding complexation (See Fig. 3B). As reported earlier [1–4], CPS/BVP and many other H-bonding complexes generally show a negative deviation from the additivity law and a tendency of having a fixed segment composition corresponding to the minimum viscosity, suggest the segments of component polymer coils pairing each other. For ionic interaction complexes, the situation is complicated. It can be seen from Fig. 4 that the curves are relatively flat, so the F_r corresponding to the maxima locates at a relatively broad range rather than a fixed value. A similar phenomenon has been reported for many ionic interaction systems, e.g. Lu and Weiss reported that SPS ionomer/SVP solutions in THF exhibited the viscosity maxima locating at a range of [SO$_3^-$]/[VP] = 1/3 to 1/2, and we also found that SSEBS triblock ionomers/SVP blend solutions showed a rather flat maximum range in viscosity versus composition curves.

3.2. Complexation in solution studied by DLS

DLS is one of the most sensitive methods for studying the association of ionomers [24–28] and polyeletrolytes [29] in solution. So far, to our knowledge, there are very few publications on the intermacromolecular complexation of ionomers in both aqueous [29] and non-aqueous media [1–3,20,21] studied by DLS. In our previous work [1–3,20,21], DLS investigations on intermacromolecular complexation because of H-bonding or ionic interaction have been successfully conducted. DLS can directly monitor the complexation based on the fact that complexation is often accompanied by the change in the hydrodynamic radius because of the interpenetration and aggregation of the unlike chains. Generally, a larger hydrodynamic radius with narrower distribution would result when a complex is formed by either the H-bonding or the ionic interaction [1–3,20,21]. It should be noted that the H-bonding complexation in polymer blend solutions often results in unstable complex dispersion and even precipitates [8]. This of course causes some difficulties in the characterization of the complexes and the complexation process. In the present study, however, ZnCPS/BVP ionic interaction complexes are

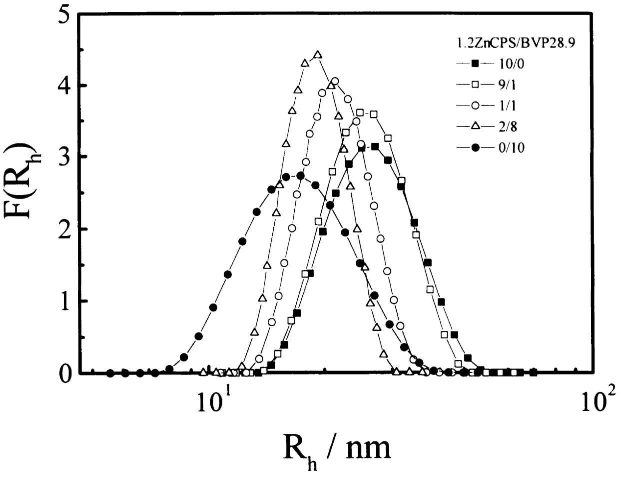


Fig. 5. Hydrodynamic radius distributions $f(R_h)$ of 1.2ZnCPS/BVP28.9 blend solutions in THF.

soluble, thus DLS can provide more reliable information on complexation.

Both Figs. 5 and 6 show the apparent hydrodynamic radius distributions $f(R_h)$ of the blend solutions versus composition. It can be seen that both 1.2ZnCPS and 7.2ZnCPS show broad $f(R_h)$ extending to about 60 and 90 nm, respectively, although their parent polystyrene possesses a narrow molecular weight distribution. This is an indication of the intermolecular self-association of the ionomers coexisting with single ionomer chains in THF. Meanwhile all the blend solutions of 1.2ZnCPS/BVP28.9 with different compositions show broad $f(R_h)$ over the size range of the two components. Further, as shown in Fig. 7, the average hydrodynamic radius ($\langle R_h \rangle$) of the blend solutions varies linearly with composition, i.e. $\langle R_h \rangle$ closely follows the additivity law. This clearly indicates that little detectable complexation takes place in the blends, as the content of the interaction site in CPS is too low.

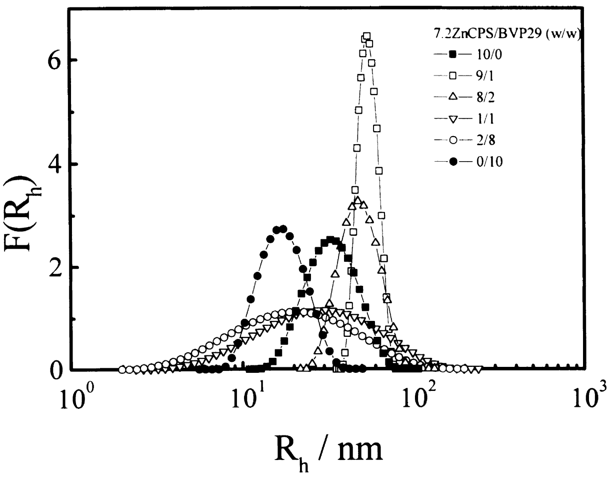


Fig. 6. Hydrodynamic radius distributions $f(R_h)$ of 7.2ZnCPS/BVP28.9 blend solutions in THF.

For 7.2ZnCPS/BVP28.9, Fig. 6 shows that $f(R_h)$ of the blends largely depends on the composition. The blend with a relatively low content of 7.2ZnCPS ($F_w = 0.2$) shows a distribution broader than both the component polymers, having a tail with R_h extending to a few hundreds of nanometers, and consequently an higher average $\langle R_h \rangle$ than that calculated by the additivity (See Fig. 7). It means that complexation between ZnCPS and BVP29 forms resulting in the coexistence of the complexes and the component polymers. As ZnCPS becomes predominant, the blends show much narrower distributions and R_h at peak position ($R_{h,\ peak}$) much larger than either 7.2CPS or BVP29. These facts directly demonstrate the occurrence of complexation. Further, as shown in Figs. 6 and 7, at $F_w = 0.9$ ($F_r = 0.73$), R_h of the blend shows the narrowest distribution and the average value $\langle R_h \rangle$ reaches about 55 nm, about double the corresponding weight average value of the independent component polymer coils. This suggests that the two kinds of component polymer coil are no longer isolated but combined. We notice that the F_r corresponding to the maximum $\langle R_h \rangle$ here is somewhat higher than that for the maximum viscosity shown in Fig. 4. This is probably because of the fact that the solution concentration for DLS (1.0×10^{-4} g/ml) is much lower than that for the viscosity measurements (2×10^{-3} g/ml). Although intuitively it is understandable that complexation depends on the concentration of the blend solution, i.e. the higher the concentration, the stronger the complexation ability, no detailed experimental data are available for discussing the question. The main reason is lack of techniques capable of monitoring complexation over a broad range of concentration, especially for the concentrated solutions.

3.3. A comparison between hydrogen-bonding complexation and ionic interaction complexation in solution

Although complexation induced by either ionic interactions or H-bonding results in the formation of the complex aggregate with much larger hydrodynamic radius than the components, they show opposite viscosity behavior. Just as we summarized in our review article [1], interpolymer complexation because of H-bonding in solutions always leads to a negative deviation from the additivity law in the plot of reduced viscosity against blend composition, but meanwhile, a substantial increase of the hydrodynamic radius compared to those of the component polymers. As an example, the results of blend solutions of 7.2CPS and BVP in butanone [2,3], where the interacting group in CPS is in acid form [2,3] but with the same content as that for ZnCPS is shown in Fig. 3B. The 7.2CPS/BVP solutions show much lower viscosity than the expected values by additivity and the larger the interacting group content, the lower the viscosity. As mentioned above, for ZnCPS/BVP in THF caused by the coordination interaction between pyridine and zinc ions, a positive viscosity deviation from the additivity law is observed. In our opinion, this striking

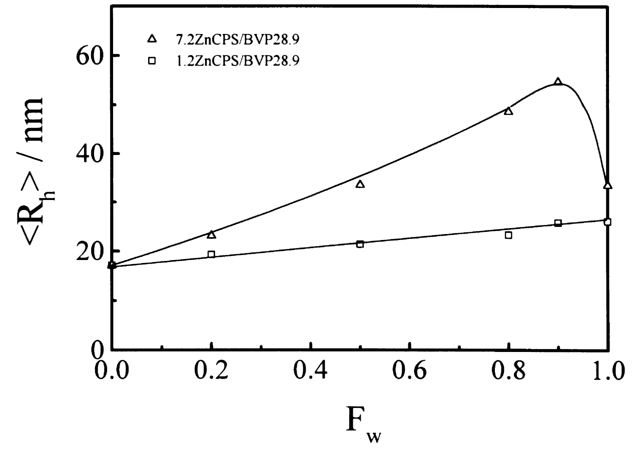
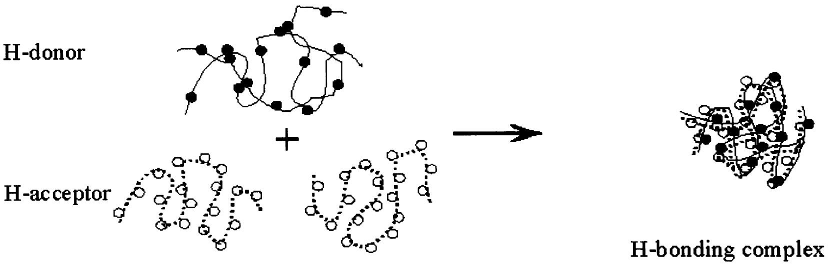


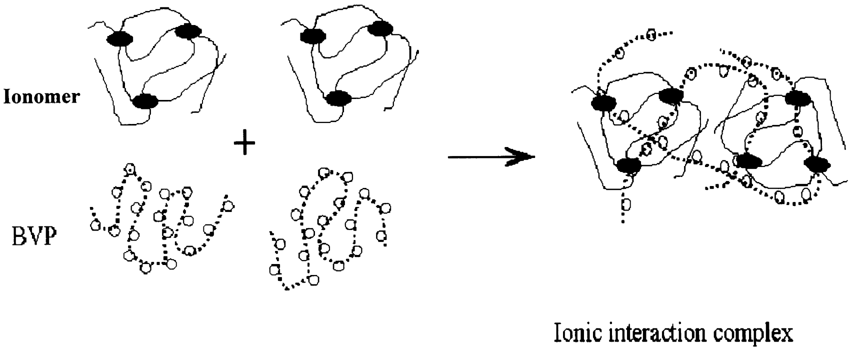
Fig. 7. Composition dependence of average hydrodynamic radius of ZnCPS/BVP28.9 blends.

difference can be attributed to the unlike microstructural characters between the ionic interaction and the H-bonding systems (Fig. 8). It is well known that an ionomer solution in a nonpolar solvent, is characteristic of the intra- and intermolecular association caused by aggregation of the ionic groups because of the great difference in polarity between the ionic groups and hydrocarbon backbones. In other words, the ionic groups in the solutions do not distribute homogeneously but concentrate in the ion-rich microdomains. It is reasonable to think that the interaction between the ligand in BVP chains and the metal ions is basically localized in the microdomains as well. Therefore, although the interactions can connect the unlike chains to form a large complex aggregate, as evidenced by a pronounced increase of $\langle R_h \rangle$, the localization of the interaction prevents the unlike chains from fully confusing and interpenetrating at a segment level. In other words, the conformation of the component polymer chains is slightly affected by the complexation, thus the complexing polymer chains can consequently retain their solvation to a certain extent, and keep soluble. When the interactions are very strong, they form gel instead of precipitates [20,21].

For the blend solutions composed of proton-donating and proton-accepting polymers, both the interacting groups, being non-ionic, do not possess sufficient contrast in polarity with the backbones, and thus distribute homogeneously in the coils in solution. Therefore, the H-bonding between the unlike chains not only makes interchain connection but also influences greatly the chain conformation, namely, it causes the unlike-segment pairing and thus the chains lose its solvation ability and collapse in the solutions. Consequently, much lower viscosity is obtained. In many cases,



Complexation due to H-bonding



Complexation due to ionic interaction

Fig. 8. A schematic presentation of the two kinds of complexation.

Table 2
T_gs (°C) for ZnCPS, BVP and the blends of ZnCPS/BVP (w/w 80/20)

	1.2ZnCPS	7.2ZnCPS	BVP4.7	BVP11.1	BVP28.9
Pure component	102	116	38	42	46
1.2ZnCPS/BVP4.7	101	/	38	/	/
1.2ZnCPS/BVP11.1	102	/	/	43	/
1.2ZnCPS/BVP28.9	102	/	/	/	46
7.2ZnCPS/BVP4.7	/	116	38	/	/
7.2ZnCPS/BVP11.1	/	107	/	47	/
7.2ZnCPS/BVP28.9			One T_g 100		

when the concentration is not very low, precipitation even occurs.

3.4. The complexation in bulk

Our investigations on complexation behavior of the blend solutions were extended to the solid state and the variation in T_g was used to evaluate the miscibility and complexation of the THF-cast blends. For all the blends with LiCPS, including that with the highest ionic interaction level we examined, i.e. 7.2LiCPS/BVP28.9, two T_gs, which are very close to those of the corresponding components, were observed. This implies that no intermolecular complexation in the blend occurs. Obviously, this result of the blends in solid state is in consistence with the solution data. Table 2 lists T_gs of the ZnCPS/BVP blends with different compositions cast from THF solutions compared to those of the component polymers. It can be seen that, when either ionic group or VP unit is at the lowest content we investigated, i.e. in 1.2ZnCPS/BVP and ZnCPS/BVP4.7 blends, two T_gs close to those of the corresponding component polymers are observed, indicating that the interpolymer interaction is not strong enough to cause phase mixing and complexation between the component polymers. However, when the interactions reach a certain level, such as in 7.2ZnCPS/BVP11.1 blends, two T_gs with substantial shifts compared to those of the component polymers are observed. Figs. 9 and 10A are the plots of DSC thermograms and the corresponding T_g versus composition for 7.2ZnCPS/BVP28.9 blends, respectively. For the pure component, a single sharp glass transition, i.e. 116°C for 7.2ZnCPS and 46°C for BVP28.9 was observed. Each of the blends, i.e. ZnCPS/BVP w/w 4/6 and 6/4 exhibits two T_gs, shifting towards each other. This means that some miscibility enhancement has been realized in the blends. In fact, at a high content, e.g. 80 wt% of 7.2ZnCPS, a single T_g can be seen, indicating that miscibility is resulted. It is remarkable to see that the polymer pairs forming complexes in solutions as evidenced by viscometry and DLS measurements, may display two T_gs. In other words, the complexation caused by ionic interaction does not necessarily lead to miscibility.

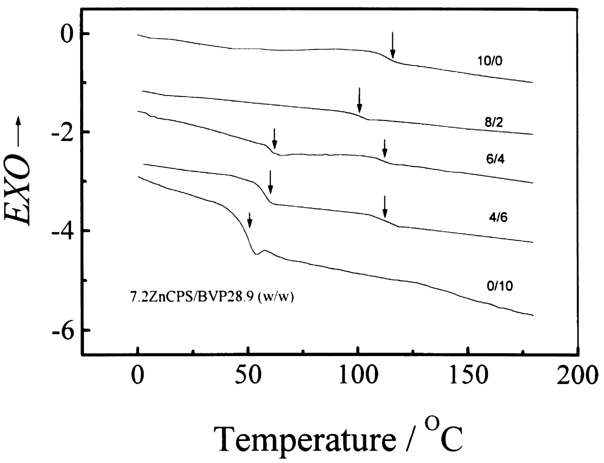


Fig. 9. DSC curves of 7.2ZnCPS, BVP28.9 and their blends at different compositions (indicated in the figure).

It is worth noting that either in solutions or in bulk, the lithium ionomers LiCPS show much weaker complexation ability with VP-containing polymers than the transition metal ionomers ZnCPS do. This result parallels with that found in *sulfonated* ionomers. Many reports [6,7,11] proved that with VP-containing polymers the alkali and alkaline earth metal sulfonates show very weak interactions, insignificant as compared with the transition metal ones. Recently, Goh et al. [30] reported that X-ray photoelectron spectroscopy (XPS) showed the development of high-binding-energy N 1s peak in Zn sulfonated PS/P4VPy but not in the Li ionomer blends. In other words, XPS reveals the existence of coordination between Zn ion and P4VPy but not between Li ion and P4VPy. In the case of polyamide used as the counter polymer, detailed spectroscopic studies including FTIR [31,32] and solid-state NMR [31,33] confirmed the legand–metal coordination between the amide nitrogen and the Zinc cations in sulfonates. However, to our knowledge, for carboxylated ionomer blends, little attention has been paid on the interaction nature by spectroscopy in the literature so far and the topic is still open. As in the case of *acid form* of sulfonated and carboxylated ionomers, the difference in their interactions with VP-containing polymers is significant. FTIR studies [34,35] showed that in the blends, the sulfonic acid groups formed sulfonate anions and the pyridine groups formed pyridium cations, basically, there is acid/base interaction between SO_3H and pyridine groups. However, for CPS/BVP blends, no IR absorption band for pyridinium ion was observed [2], which implies

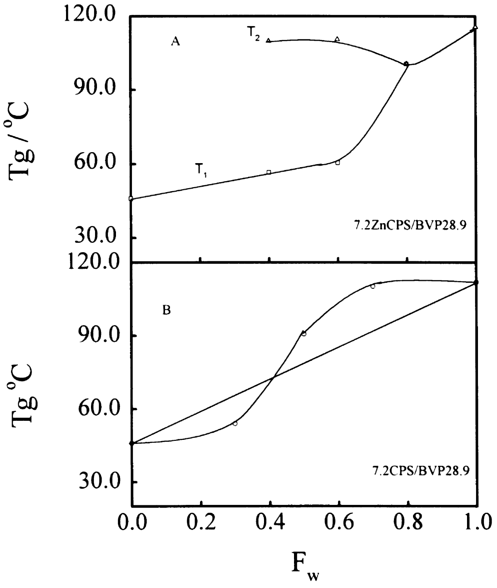


Fig. 10. Composition dependence of T_g for 7.2ZnCPS/BVP28.9 (A) and 7.2CPS/BVP28.9 blends (B).

that hydrogen-bonding interaction dominates between COOH and pyridine groups.

It is generally accepted that the ion pairs of an ionomer aggregate forming ion-rich regions such as mutiplets and clusters in solid state [36,37]. For ZnCPS/BVP blends, we are inclined to think that the ionic interaction mainly exists in the ion-rich regions in solid state. As we pointed out above, in solutions, a relatively low ionic interaction level may be enough to physically cross-link the unlike chains, namely forming complex, but this localized interactions may not be strong enough to result in mixing of unlike chains at a segmental level. In fact, only at a very high level of ionic interaction, e.g. in 7.2ZnCPS/BVP28.9 blends (8/2 w/w), the unlike chains can be completely miscible, and only one T_g is observed.

H-bonding complexes [1–4] show different behavior. For example, as shown in Fig. 10B, for the blend of 7.2CPS/BVP28.9 with the same contents of the functional groups as those of 7.2ZnCPS/BVP28.9, over the whole composition range, only one T_g is obtained [2,3]. Further, when 7.2CPS is predominant, T_g is apparently higher than the values expected by the additivity law, e.g. 7.2CPS/BVP28.9 (7/3 w/w) shows a T_g of 110°C versus the weight average value 94°C. In fact, in all the polymer pairs with hydrogen bonding we studied [1], complexation exclusively leads to one glass transition temperature. In our opinion, because the interacting sites are randomly distributed along the polymer chains, the interaction causes polymer segment pairing and chain interpenetrating, and consequently one T_g, provided it is strong enough. At a high H-bonding level, chains become rigid showing even higher T_g. In short, the difference in the microstructure between the ionic interaction and H-bonding interaction systems is responsible for their difference in the phase mixing and T_g behavior in solid states.

4. Conclusion

Intermacromolecular complexation behavior between ionomers based on CPS and pyridine-unit containing copolymers have been investigated in solution and in bulk. It shows that the transition metal salts ZnCPS can form complexation with BVP at a relatively high level of specific interaction, reflected in the enhanced viscosity, increased hydrodynamic radius with a narrow distribution in solution, as well as two T_gs shifting towards each other or even only one T_g at a high specific interaction level in solid state. In contrast, the H-bonding complexation usually gives rise to a decrease in viscosity, an increase in the hydrodynamic radius and the narrowing hydrodynamic radius distribution in solution, and only one, often increased T_g in solid state. These differences between the H-bonding complexation and ionic interaction complexation can be attributed to that the ionic interacting groups aggregate in the ion-rich microdomains while the H-bonding sites are randomly distributed.

Acknowledgements

We would like to thank the National Basic Research Project-Macromolecular Condensed State Programme, the National Natural Science Foundation of China (Grant No. 59773023), and the Doctoral Programme Foundation of Institution High Education for support of this research.

References

[1] Jiang M, Li M, Xiang M, Zhou H. Adv Polym Sci 1999;146:121.
[2] Zhu I, Jiang M, Liu I, Zhou H, Fan L, Zhang Y. J Macromol Sci, Phys B 1998;37(6):827.
[3] Zhu L. MSc thesis, Fudan University, 1996.
[4] Tsuchida E, Abe K. Adv Polym Sci 1982;45:1.
[5] Lunberg RD, Peiffer DG, Phillips RR. United States Patent 4480063, 1984.
[6] Peiffer DG, Duvdevani I, Agarwal PK, Lunberg RD. J Polym Sci Polym Lett 1986;24:581.
[7] Lunberg RD, Phillips RR. J Polym Sci Polym Phys 1989;27:245.
[8] Feng K, Zeng Z, Ouyang W, Li Z. J Appl Polym Sci 1996;61:729.
[9] Pan Y, Huang Y, Liao B, Cong G, Leung LM. Eur Polym J 1998;34:207.
[10] Pan Y, Huang Y, Cheng M, Cong G, Leung IM. Eur Polym J 1998;34:212.
[11] Lu X, Weiss RA. Macromolecules 1991;24:5763.
[12] Bakeev KN, MacKnight WJ. Macromolecules 1991;24:4575.
[13] Horrion J, Jerome R, Teyssie Ph. J Polym Sci, Polym Lett Ed 1986;24:69.
[14] Horrion J, Jerome R, Teyssie Ph. J Polym Sci, Polym Chem 1990;28:153.
[15] Russell TP, Jerome R, Charlier P, Foucar M. Macromolecules 1988;21:1709.
[16] Shao L, Weiss RA, Lundberg RD. J Polym Sci, Polym Phys 1995;33:2083.
[17] Weiss RA, Shao L. Macromolecules 1992;25:6370.
[18] Weiss RA, Shasongko S. Macromolecules 1991;24:2271.
[19] Register RA, Weiss R, Li C, Cooper S. J Polym Sci. Polym Phys 1989;27:1911.
[20] Jiang M, Liu W, Wu C, Woo K. Polymer 1997;28:405.

[21] Liu W, Jiang M. Chem J Chin Univ 1997;18:309.
[22] Hird B, Eisenberg A. J Polym Sci Polym Chem 1993;31:1337.
[23] Chu B. Laser light scattering: basic principles and practice. 2nd ed. London: Academic Press, 1991.
[24] Lantman CW, Macknight WJ, Peiffer DG, Sinha SK, Lundberg RD. Macromolecules 1987;20:1096.
[25] Pedley AM, Higgins JS, Peiffer DG, Burchard W. Macromolecules 1990;23:1434.
[26] Hara M, Wu J, Lee AH. Macromolecules 1988;21:2214.
[27] Hara M, Wu J. Macromolecule 1988;21:402.
[28] Wu C, Woo K, Jiang M. Macromolecules 1996;29:5361.
[29] Dautzenberg H, Koetz J, Linow KJ, Phillips B, Rother G. In: Dubin P, editor. Macromolecular complexes in chemistry and biology, Berlin: Springer, 1994 (part 2, chap. 8, p. 119).
[30] Goh SH, Lee SY, Zhou X, Tan KL. Macromolecules 1998;31:4260.
[31] Feng Y, Schmidt A, Weiss RA. Macromlecules 1996;29:3909.
[32] Lu X, Weiss RA. Macromolecules 1992;25:6185.
[33] Kwei TK, Dai YK, Lu X, Weiss RA. Macromolecules 1993;26:6583.
[34] Sakurai K, Douglas EP, Macknight WJ. Macromolecules 1992;25:4506.
[35] Smith P, Eisenberg A. Macromolecules 1994;27:545.
[36] Eisenberg A. Macromolecules 1970;3:147.
[37] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23:4098.