Polymer Vol. 38 No. 2, pp. 405-412, 1997
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

S0032-3861(96)00519-8

Complexation of SEBS-based ionomers with pyridine-unit-containing copolymers in solution and bulk

Ming Jiang* **and Weifeng Liu**
Institute of Macromolecular Science and Laboratory of Macromolecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

and Chi Wu and KaFai Woo
Chemistry Department, The Chinese University of Hong Kong, Shatin, Hong Kong
(Received 17 October 1995; revised 22 April 1996)

This paper studies complexation behaviour between block ionomers with metal sulfonate groups and pyridine-group-containing copolymers, i.e. poly(styrene-*co*-4-vinyl pyridine) (STVP) and poly(methyl methacrylate-*co*-4-vinyl pyridine) (MVP) in both solution and bulk. The block ionomers based on poly(styrene-*b*-ethylene-*co*-butene-*b*-styrene) (SEBS) with metal sulfonate groups were prepared by sulfonation of SEBS followed by neutralization. In the blend solutions in tetrahydrofuran, intercomponent complexation is evidenced by an unusual increase in the reduced viscosity relative to the solutions of SEBS and the copolymers. This complexation was observed by dynamic light scattering (DLS) measurements to take place at concentrations as low as 0.01 $\mathrm{g\,dl^{-1}}$. DLS also shows the coexistence of two kinds of complex differing considerably in size, which are formed from STVP with single block ionomers and block ionomer aggregates, respectively. Among the different metal salts of alkali, alkaline earth and transition metals studied, copper and nickel show the greatest capability of complexation. In the solvent-cast blends of ionomer/MVP and ionomer/STVP, T_g is much higher than expected for the usual miscible blends, and varies with the blend composition in a way similar to the reduced viscosity of the blend solutions, with a similarly located maximum; this implies that the apparent increase in T_g of the blends is caused by complexation which occurs at dilute solution and is preserved in the casting process. Copyright © 1996 Elsevier Science Ltd.

(Keywords: block ionomer; SEBS; association)

INTRODUCTION

Recently we reported[1-3] the results of viscometry and dynamic light scattering (DLS) on solutions of metal-sulfonated SEBS, i.e. hydrogenated poly(styrene-*b*-butadiene-*b*-styrene), in the non-polar solvent tetrahydrofuran (THF) for exploring the behaviour of intramolecular and intermolecular associations due to aggregation of the ion pairs. This paper extends the work to the solutions and bulk of a series of blends, each of which comprises one SEBS-based block ionomer and one pyridine-unit-containing polymer. The main relevant results presented in the paper demonstrate complexation between the blend constituents, both in solutions and the bulk.

Although to our knowledge there are no published reports on the properties of solutions composed of both a SEBS-based block ionomer and an amine-containing polymer, to understand the interaction between a random ionomer with groups of sulfonic acid or metal sulfonate and amine-containing polymers has long been a recognized problem, and there has been increasing interest in recent years. Peiffer *et al.*[4] studied the melt viscosity of blends composed of sulfonated ethylene–propylene terpolymer (SEPDM) and poly(styrene-*co*-4-vinyl pyridine) (STVP) in which VP is always the minor unit. Their results showed that the transition metal salt of SEPDM resulted in higher melt viscosities than the comparable blends containing non-transition metal salts. This was attributed to the formation of a coordinate complex between the transition metal salt of SEPDM and the vinyl pyridine units. Later, some viscosity data for the solutions of the same blends in xylene were reported[5]. A maximum in the solution viscosity *versus* composition curve of the zinc salt of SEPDM and STVP was found at [VP]/[sulfonate] = 1, which was regarded as a complex stoichiometry. Blend solutions of STVP and zinc-sulfonated polystyrene in xylene were studied, which also showed complexation between the constituents, as evidenced by gelation. In polar solvents such as dimethyl formamide (DMF), complexation between STVP and metal-sulfonated polystyrene was observed by Lu and Weiss[6] by studying the reduced viscosity of the solutions as a function of the blend compositions. A maximum in the viscosity curve was found at [VP]/[sulfonate] = 6/1, quite different from that found in the

---

* To whom correspondence should be addressed

non-polar solvent. This difference was believed to be caused by differences in the complexation mechanisms in polar and non-polar solvents. In addition, it was found that the complexation may lead to abnormal viscosity–pressure dependence. Cook *et al.*[7] reported that the solutions of zinc-sulfonated polystyrene and STVP in THF showed an intrinsic viscosity decrease with pressure. The apparent molecular weight estimated from the viscosity data decreased by about 29%, as the pressure increased from ambient pressure to 10 kbar, whereas such a decrease was not seen in the non-associating analogues. These facts prove that there are pressure-driven changes in the degree of association.

Fluorospectroscopy[8] was employed in exploring the complexation by measuring the excimer emission of a hydrophilic fluorescence probe of a pyrene derivative with four sodium sulfonate groups. In solutions of sulfonated polystyrene and poly(ethyl acrylate-*co*-4-vinyl pyridine) (EtAc4VP) in THF, concentration-dependent excimer fluorescence, which appears when the contents of the functional groups reach a certain level, indicates the occurrence of polar interactions as a result of proton transfer from the sulfonic acid to the nitrogen of the pyridine.

Besides pyridine-unit containing copolymers, some polymers containing aliphatic amine groups were used as the blend counterpart of the sulfonated polymers. For example, Wang *et al.*[9] studied solutions of zinc-sulfonated polystyrene and poly(isobutyl methacrylate-*co*-t-butyl aminoethyl methacrylate) in the polar solvent of *N,N*-dimethyl acetamide by viscometry and light scattering. The reduced viscosity of the mixed solutions was much larger than those of the components and showed more apparent shear–thinning effect. This could be attributed to complexation between zinc ions and nitrogen in amine groups. This complexation was completely destroyed by adding a small amount of amine compounds, because these added amine molecules supplant the amine groups in the copolymers to form complexes with the ions.

EXPERIMENTAL

Materials

The preparation and characterization of a series of metal-sulfonated SEBS have been described in detail elsewhere[3]. SEBS-based ionomers were prepared from SEBS (G1652, Shell Co.), with respective molecular weights of the middle block, i.e. the random copolymer chain of ethylene and butene, and end blocks of styrene being 37 500 and 7 500. Sulfonation of SEBS was performed using fresh acetyl sulfate as the agent. The product was then treated with different metal acetates in ethanol for neutralization, producing the corresponding block ionomers. Our nomenclature for the block ionomers is illustrated by the example '6.9Cu-S-SEBS', which we use to label copper-sulfonated SEBS with 6.9 mol% ion groups based on styrene blocks. Preparation of copolymers of STVP and poly(methyl methacrylate-*co*-4-vinyl pyridine) (MVP) was conducted by free radical polymerization in THF under nitrogen using azodiisobutyronitrile as the initiator. The copolymer was precipitated in petroleum ether and then washed and dried under vacuum at 70°C for a week. The molar contents of 4-VP in the copolymers were measured by nitrogen analysis. Size exclusion chromatography was used to measure the molecular weights of the copolymers, calibrated with polystyrene standards. The results are listed in *Table 1*.

Preparation of blends and d.s.c. measurements

THF solutions of an ionomer and a copolymer 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 80°C for a week, then at 130°C for half a day. D.s.c. measurements were made with a Shimadzu DSC-50. The first run started when the sample was cooled to the desired temperature (~ -100°C) and heated at rate of 20°C min^{-1} until 200°C. Then the sample was quenched to about -100°C to start the second run. The data for the second run were recorded, and are the data used in this paper. The temperature corresponding to the half change in the heat capacity C_p was adopted as the glass transition temperature T_g.

Dynamic light scattering

Normally, a precise intensity–intensity correlation function $G(t,q)$ is measured. The linewidth distribution $G(\Gamma)$ can be obtained from $G(t,q)$ by the Laplace inversion and can be further converted to the translational diffusion coefficient distribution $G(D)$. The z-distribution of the hydrodynamic radius $f_z(R_h)$ can be obtained using the Stokes–Einstein equation $R_h = k_BT/6\pi\eta D$. Finally, the weight and number distributions of the hydrodynamic radius can be further calculated since $f_w(R_h) \propto f_z(R_h)/M$ and $f_n(R_h) \propto f_w(R_h)/M$.

A modified commercial dynamic laser light scattering (DLS) spectrometer (ALV/SP-150 equipped with an ALV-5000 digital time correlator) was used with a solid state laser (output power 400 mW and wavelength 532 nm) as the light source. The incident light beam was vertically polarized with respect to the scattering plane and the light intensity was regulated with a beam attenautor so as to avoid possible localized heating in the light-scattering cuvette. In our present set-up, the coherent factor β in the DLS instrument is about 0.87, a rather high value for a DLS spectrometer capable of working in both static and dynamic modes simultaneously. This is one of the reasons why we were able to carry out the DLS study of an extremely dilute solution with a good signal-to-noise ratio. The typical long-term temperature stability inside our DLS sample holder was 25.0 ± 0.2°C. The solution samples were prepared by dissolving the block ionomers in THF followed by filtration with 0.5 or 0.1 μm membranes.

RESULTS AND DISCUSSION

Complexation studied by viscometry

Table 1 Characterization data of copolymers of STVP and MVP

Sample	M_n	M_w	M_w/M_n	[VP] (mol%)
STVP	14 600	23 800	2.24	13.3
MVP	16 300	25 500	1.56	14.8

Viscometry is one of the simplest and most practical techniques for exploring the association and complexation of polymer solutions. In dilute solutions of a polymer pair in common solvents, the reduced viscosity is often close to the sum of the reduced viscosities of the components, thus indicating spatial independence of the component polymer coils in the solution. However, positive or negative deviations from additivity may occur, which has been taken as an indication of intercomponent complexation. In this study, blend solutions in THF with a fixed total concentration of 1 wt%, composed of one of a series of block ionomers with different counterions, Na^+, Mg^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, and one of the copolymers, i.e. STVP or MVP, were measured for reduced viscosity over the entire range of blend composition. Some typical results, i.e. the data for Na and Ni block ionomers, are shown in *Figures 1* and *2* respectively. The most remarkable feature of this series of data is the unusual increase in the reduced viscosity over the expected value from additivity. This fact is a clear indication of polymer–polymer complexation in the solutions. For the purpose of exploring the effect of the choice of cation, the maximum increase in the reduced viscosity, $\Delta\eta$, defined as the difference between the maximum and the weight average values in the viscosity *versus* composition curve, for each blend solution is listed in *Table 2*.

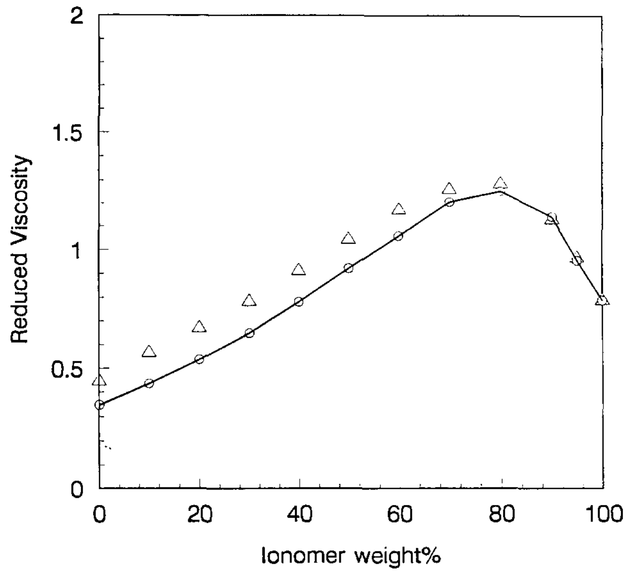

Figure 1 Reduced viscosity of blend solutions of 6.9Na-S-SEBS/STVP (○) and 6.9Na-S-SEBS/MVP (△) in THF (1 wt%) *versus* the blend composition (ionomer content in wt%)

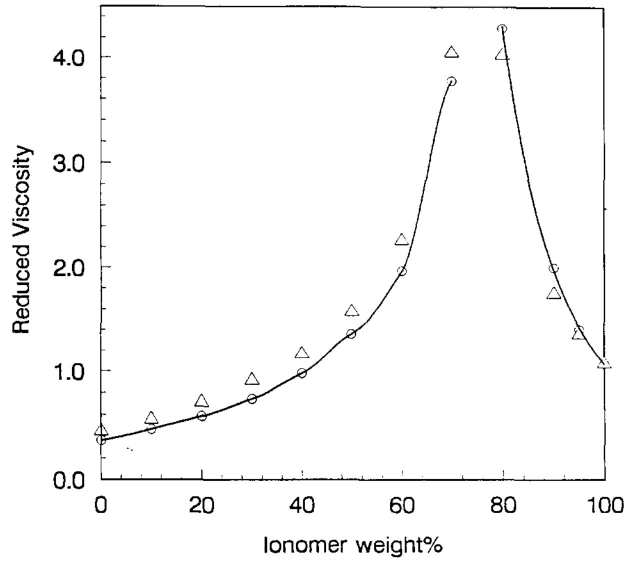

Figure 2 Reduced viscosity of blend solutions of 6.9Ni-S-SEBS/STVP (○) and 6.9Ni-S-SEBS/MVP (△) in THF (1 wt%) *versus* the blend composition (ionomer content in wt%)

Among the counterions of alkali, alkaline earth and transition metals studied, it is not surprising that the transition metals, especially nickel and copper, show the greatest capability for complexation (*Figure 2*). The complexes formed from nickel and copper ionomers remain soluble over a broad composition range, while gelation occurs in the ionomer/copolymer range from 60/40 to 90/10. In fact, many years ago, it was reported that poly(4-vinyl pyridine) formed a complex with zinc halide in which two pyridine units coordinated with one zinc ion[10]. In recent years, Belfiore *et al.*[11] studied a series of blends composed of pyridine-containing polymers and transition metal salts by a combination of techniques, from which convincing evidence was obtained for metal–ligand coordination between the lone-pair electrons of the nitrogen atom in pyridine and nickel or zinc ions. This coordination was found in our laboratory[12,13] to be the driving force for compatibilization of ionomer blends composed of two different ionomers with identical charge. The copolymers of STVP and poly(butyl methacrylate-4-vinyl pyridine), having in common the minor component VP (~ 13 mol%), are incompatible. However, apparent compatibilization was observed when a small amount of transition metal acetate was mixed in the blends as a result of coordination between pyridine units from both copolymer chains with nickel ions. Together with the results in the literature, the fact that the block ionomers of nickel and copper show the greatest level of complexation strongly suggests that coordination between pyridine and metal ions is the main mechanism for the complexation in the present blend solutions in non-polar solvents. Since the blend solutions with sodium and magnesium counterions also show some viscosity increase, but not as much as the transition metals, other mechanisms such as simple dipole–dipole interaction or ion–dipole interaction cannot be excluded.

A common feature of the blend solutions under consideration which deserves special mention is that, for each ionomer, the two kinds of blend with the counterparts of STVP and MVP have very similar viscosity composition curves with peaks at about the same composition. This not only makes the results convincing but also indicates that the inherent thermodynamic repulsion between unlike chains in these systems with strong specific interactions is not important for complexation. Lu and Weiss[6] have emphasized this role when they studied the complexation behaviour between pyridine-containing and sulfonated polymers. They deliberately employed a polymer pair of STVP and sulfonated polystyrene, both with predominately polystyrene backbones, so as to avoid the repulsion effect between unlike segments.

A more complicated problem in these systems concerns the complex composition, usually defined as

Table 2 Data related to the reduced viscosity of solutions of STVP and ionomers with different cations. $([SO_3^-]/[VP])_{max}$ and $([M]/VP])_{max}$ denote the molar ratios of SO_3 metal ions in ionomers to pyridine unit in STVP at the maximum reduced viscosity

Counterion	Na^+	Mg^{2+}	Mn^{2+}	Co^{2+}	Zn^{2+}	Ni^{2-}	Cu^{2+}
Concentration (mol%)	6.9	6.9	6.9	6.9	6.9, 8.4	6.9	6.9
$\Delta\eta$	0.6	1.0	0.9	1.9	2.0, ∞	∞	∞
$([SO_3^-]/[VP])_{max}$	1/2	1/2–1/1	1/2–1/1	1/2	1/2	1/2	1/2
$([M]/[VP])_{max}$	1/2	1/4–1/2	1/4–1/2	1/4	1/4	1/4	1/4

the composition corresponding to the peak in the viscosity–composition curve. *Figures 1* and *2* show that the complex compositions for different ions are all located around an ionomer/copolymer (w/w) ratio of 80/20. A close examination, by plotting the reduced viscosity against the relative molar fraction of SO_3^- in the total functional groups, leads to the results shown in *Table 2*. Two typical cases, magnesium and nickel, are also illustrated in *Figures 3* and *4*. The data in *Table 2* show that for most systems the molar ratio between the metal ions and VP units at the maximum viscosity, [M]/[VP], is about 1/4, while for magnesium and manganese the ratio, which is not easy to determine due to the curves being rather flat, is between 1/2 and 1/4. As stated above, the coordination number of pyridine to zinc, nickel, etc., in the blends of the polymer and transition metal salts[10] was found to be 2. Thus, roughly speaking, our complex systems of block ionomers and metal ions require more pyridine in relation to ions for complexation. As there are no reports on block ionomer complexation in the literature, comparison can only be done with some complexation data between sulfonated polymers based on polystyrene and ethylene propylene diene monomer (EPDM) and pyridine-containing random copolymers. Peiffer *et al.*[4] found that in STVP/sulfonated EPDM/xylene, the complex involves only one VP per sulfonated groups. However, the viscosity data suggest that for sulfonated polystyrene and STVP in DMSO[5] the ratio is about 1/6. In a detailed study on reduced viscosity of STVP and sulfonated polystyrene (sodium and zinc) in the polar solvent DMF by Lu *et al.*[6], it is reported that the viscosity maximum corresponds to sulfonated polystyrene/VP, at about 1/6. It was proposed in that paper that the competition between the solvent DMF and the VP for complexation with the sulfonated ion might be responsible for the high VP composition. The only data in the paper dealing with solutions in the non-polar THF are for STVP and sulfonic acid modified polystyrene (2.3 and 5.0 mol%, respectively). Both of these cases show viscosity maxima located at an [acid]/[VP] composition of about 1/2 to 1/3, similar to what we found, even though acid–base interaction via proton transfer should be the complexation mechanism there. For STVP and sulfonated polystyrene in non-polar hydrocarbon solvents, no data are available for estimating the complex composition, since it was reported that in xylene, mixing of the component solutions resulted in gelation[5]. In short, the stoichiometry in polymer–polymer complexation is rather a complex problem. It depends first on the complexation mechanism, the distribution of functional sites on the chains, steric hindrance around the active sites and chain conformation, etc. Up to now, the data accumulated in the literature have not been enough to make general rules.

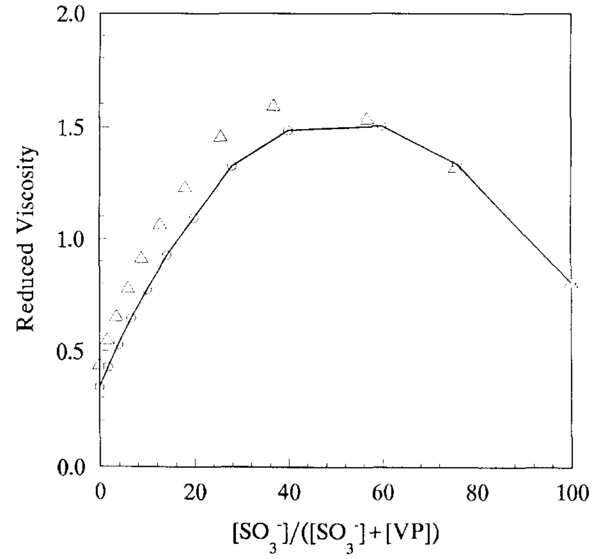

Figure 3 Reduced viscosity of blend solutions of 6.9Mg-S-SEBS/STVP (○) and 6.9Mg-S-SEBS/MVP (△) in THF (1 wt%) versus the molar fraction of ion groups $([SO_3^-]/([SO_3^-]+[VP])$

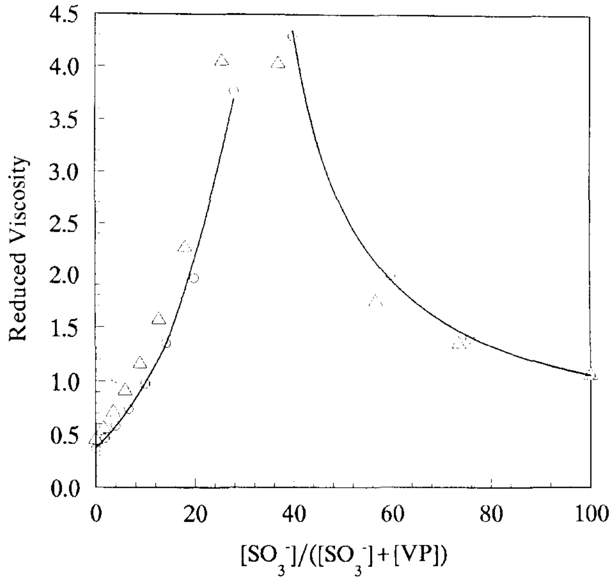

Figure 4 Reduced viscosity of blend solutions of 6.9Ni-S-S-SEBS/STVP (○) and 6.9Ni-S-SEBS/MVP (△) in THF (1 wt%) *versus* the molar fraction of ion groups $([SO_3^-]/([SO_3^-]+[VP]))$

Some early work reported that macromolecular complexes often have 1/1 or a nearly equimolar composition; however, they are mostly for polymer pairs soluble in water having one active site for each repeating unit in both constituent polymers[14].

Obviously, this conclusion cannot be applied to the present cases in which only small numbers of the repeating units are attached by the functional groups. In a series of our recent works[15–17], we have concentrated on complexation due to hydrogen bonding for blends composed of poly(methyl methacrylate) (PMMA), in which each unit has a carbonyl group as a proton acceptor, and modified polystyrene (PS(OH)) with an introduced hydroxyl group as a proton donor. The reduced viscosity of the blend solution in toluene is always lower than the weight-average value and there is a maximum in the reduced viscosity *versus* composition plot, provided the hydroxyl content in PS(OH) is higher than about 5 mol%. The blend composition corresponding to the minimum is regarded as the fixed mean stoichiometry of the complex. It is interesting to note that the complex composition, expressed as the unit molar ratio of PS(OH) to PMMA, at the viscosity minimum, decreases as the hydroxy content in PS(OH), and hence the hydrogen bonding density, increases. When the hydroxyl content in PS(OH) increases to about 24 mol%, the complex composition reaches the equimolar ratio of 1/1. It means that in the complexes each PMMA unit has its own sole counterpart of the polystyrene unit, provided the hydrogen bonding density between the chains is high enough. For the present case of solutions of ionomers and copolymers, since the block ionomers themselves display intermolecular association, as discussed elsewhere[1–3], we are inclined to think that the complexes hardly possess a fixed, mean stoichiometry.

Two kinds of viscosity–composition dependence

There are at least two apparently opposite kinds of results in the literature concerning the composition dependence of the reduced viscosity of blend solutions capable of forming complexes. The first is that the reduced viscosity of the blend solution is always smaller than the value expected from additivity and that the curve shows a minimum. The second is that the blend reduced viscosity is always larger than the calculated weight-average value and shows a maximum. Many hydrogen-bonding complexes belong to the first type[14–16]. It seems surprising that for so substantial a disparity in the experimental phenomena there has not been, to our knowledge, any detailed interpretation put forward in the literature. Based on our practical experience, we would like to suggest the following. In the case of the system showing a minimum, the complex is mostly in the form of the relatively 'tight' chain-to-chain structure that accompanies coil collapse, and precipitation may then occur if the concentration and/or interaction intensity is high enough. The precipitate frequently preserves its stoichiometry of the complex, which is often 1/1, formed in the solution (*Figure 5a*). However, in the second case, interactions between functional groups may result in loose, cross-linking structures with no well-defined composition. Therefore, the solution viscosity increases and gelation takes place when the concentration and/or interaction site density increases further (*Figure 5b*). Obviously, the present complexes formed between the ionomers and pyridine-containing copolymers belong to the latter case. In addition, as confirmed by the results of DLS, the ionomer itself possesses intermolecular association[1–3] even at low concentrations, to form chain aggregates; therefore, it is reasonable to expect that the complex has a rather complicated, ill-defined structure. Obviously, this argument cannot be applied to complexation of either polyelectrolytes or ionomers in polar solvents, since the viscosity behaviour of these cases is rather complicated due to the effect of charge repulsion.

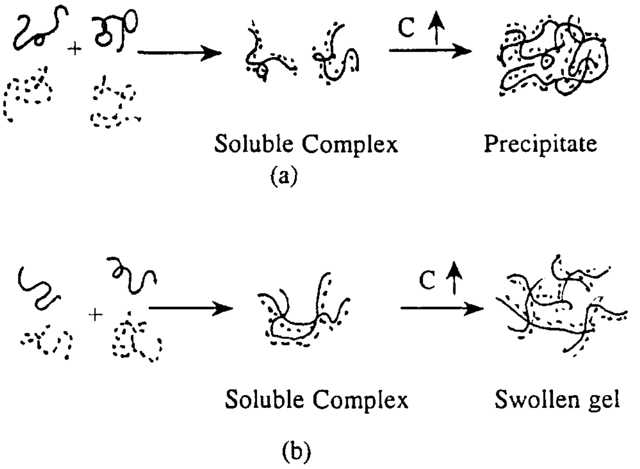

Figure 5 Schematic representations of (a) complexation with viscosity decrease and (b) complexation with viscosity increase

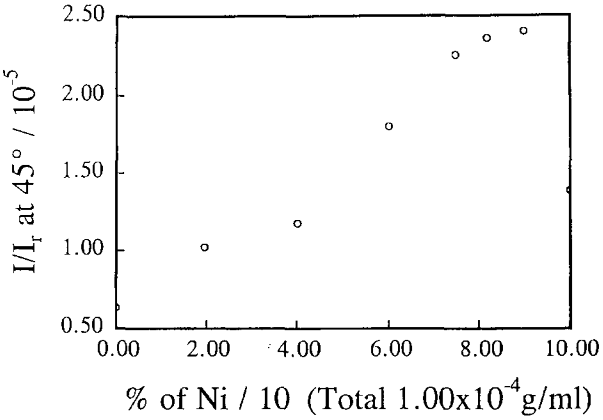

Figure 6 Relative scattering intensity of blend solutions of 6.9Ni-S-SEBS/STVP in THF observed at 45° as a function of blend composition (ionomer content in wt%), I and I_r are the intensities of the solutions and reference, respectively

Complexation studied by DLS

Nickel-sulfonated SEBS, which has been found to be most capable of intermolecular association and complexation with pyridine-containing copolymers, was chosen for our DLS studies. The measurements were made on mixed solutions of 6.9Ni-S-SEBS and STVP in THF with a total concentration of 0.01 g dl^{-1}, over the entire relative composition range. *Figure 6* shows the relative scattering intensity as a function of the composition. A substantial increase in intensity is observed when a small amount (10 wt%) of STVP is added to the ionomer solution. The intensity is much higher than that of the average values over the whole composition range. This apparent intensity increase implies that in the mixed solutions the two kinds of constituent molecule are, at least partially, no longer independent; instead, they form some kind of larger intercomponent aggregates.

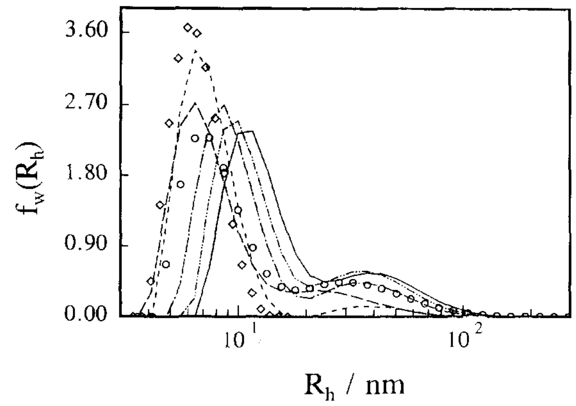

Figure 7 R_h weight distributions of the blend solutions of 6.9Ni-S-SEBS/STVP (50/50) in THF at different polymer pair compositions: 100/0 (○), 90/10 (—), 80/20 (– –) 60/40 (· –), 40/60 (– –), 20/80 (- - -), 0/100 (◇)

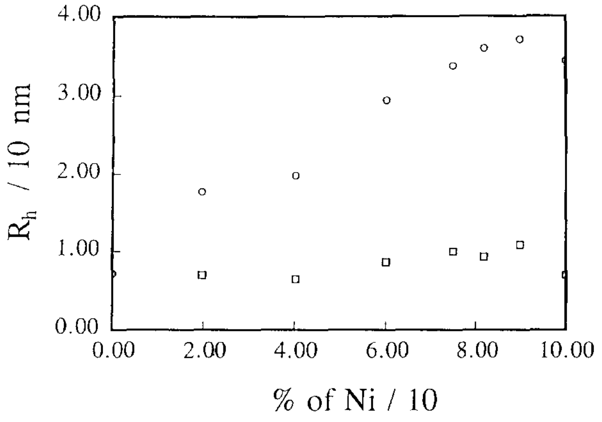

Figure 8 R_h of the complex formed from ionomer aggregates of 6.9Ni-S-SEBS and STVP (○) and R_h of the complex from the single ionomer and STVP (□) as a function of the blend composition (ionomer in wt%)

Figure 7 shows the weight distributions of the hydrodynamic radius R_h of STVP, the nickel sulfonated SEBS and their blends in THF. As expected, the random copolymer STVP possesses a one-peak distribution with an average R_h of 8 nm, while 6.9Ni-S-SEBS, just as we reported elsewhere[1-3] for 6.9Mn-S-SEBS, shows a bimodal distribution, indicating the presence of both single chains and chain aggregates. From the curves, two average R_h values, one for the single chains and one for the aggregates can be calculated, and are shown in *Figure 8*. The most important fact revealed by the data is that either the single chains or the aggregates have sizes higher than expected by additivity. In particular, for the mixed solutions, in which the ionomer is the dominant (80–90 wt%) component, both R_h values are higher than the values for either the ionomer or the copolymer alone. This result demonstrates that both single ionomer chains and their aggregates are capable of combining further with STVP molecules forming a 'simple complex' and a 'aggregate complex', respectively. Both R_h *versus* composition curves are asymmetrical, with a maximum located in the ionomer/STVP range from 80/20 to 90/10. This is close to but higher than that estimated from the viscosity measurement. It should be noted that this was obtained for the solution at a concentration of 0.01 g dl^{-1}, two orders of magnitude less than in the viscosity measurements. Considering that the average size of the aggregate complex is larger than that of the simple complex by a factor of a few decades, and the weight fraction of the former is relatively small as shown in *Figure 7*, it is believed that the number of aggregate complex molecules is very small, and thus most of the STVP and the ionomer molecules are present in the form of simple complexes, which may have a rela-tively defined complex composition.

Bakeev *et al.*[8] have reported some results of a fluorescence study on the complexation in THF solutions of a sulfonated polystyrene and a copolymer of ethyl acrylate and 4-vinyl pyridine (EAVP), in which a water-soluble pyrene substitute was employed as a probe for the formation of ionic aggregates. A dramatic increase in excimer emission was found for the mixed solution when the concentration was increased to about 0.1 g dl^{-1}. Concentration-dependent excimer fluorescence indicates the occurrence of polar interactions as a result of proton transfer from the SO_3H group to the pyridine. This result is in general agreement with that we obtained from DLS. However, DLS not only detects the complexation at even lower concentrations, owing to its sensitivity, but is also able to detect and differentiate complexation associated with single chains and aggregates of the ionomers, while the fluorescence study only provides an overall picture of the complex.

Complexation in bulk blends

The study of complexation in THF solutions of the block ionomers and random copolymers has been extended to solid state blends. A series of blends composed of the SEBS-based ionomers and their counterpart STVP or MVP were prepared by solvent casting from methanol/toluene (10/90). The cast dried films were studied by d.s.c. with an emphasis on the variation of the glass transition temperature as a function of the blend composition. In this paper, only the results for 6.9Ni-S-SEBS/MVP and 6.9Cu-S-SEBS/MVP are discussed. The d.s.c. trace of the parent resin, SEBS, is fairly complicated, showing a glass transition at about −41°C, which is associated with the soft phase of EB blocks. This transition is partially overlapped by a rather broad endothermic region extending to about 40°C. The latter is probably caused by a melting process of the partial, imperfect crystalline of the EB chain[18]. The glass transition of the hard phase of polystyrene blocks covers a broad temperature range, which makes an accurate estimation of T_g difficult. The T_g of the polystyrene phase was found to be about 80°C, much lower than that for homopolymeric polystyrene. The low molecular weight (7500) of polystyrene blocks and the influence of the soft chain EB chemically bonded to PS on its mobility may be the main reasons for the broadening and lowering of the glass transition temperature of the polystyrene phase of SEBS. This complicated d.s.c. curve of SEBS is in agreement with those reported in the literature[19].

The copper ionomer 6.9Cu-S-SEBS shows almost the same d.s.c. curve as its parent block copolymer except for a slightly higher T_g of the hard phase. The d.s.c. curves for blends of Cu-S-SEBS and MVP in various ratios, displayed in *Figure 9*, indicate that the T_g of the soft

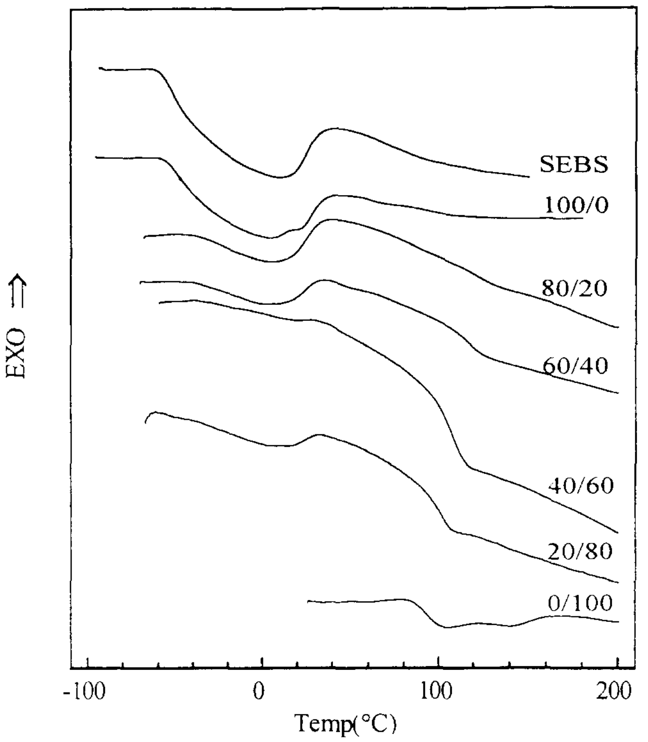

Figure 9 D.s.c. curves of 6.9Cu-S-SEBS, MVP and their blends at different compositions (indicated in the figure)

phase EB is not affected by the addition of MVP. This is understandable because complexation takes place only in the hard phase. The most important result from the d.s.c. measurements concerns the variation of the T_g of the hard phase with the blend composition. The data for the blends with nickel and copper ionomers are listed in *Table 3*.

The d.s.c. results for 6.9Ni-S-SEBS, MVP and their blends show that the T_g of the hard phase over the whole blend composition range is much higher than for either 6.9Ni-S-SEBS or MVP alone. For the blend 6.9Ni-S-SEBS/MVP 80/20, the T_g is as high as 121°C, or some 30°C higher than expected from additivity. In addition, with respect to the T_g increase, the blends of the ionomers with the copolymer STVP have been found to show the same behaviour.

The Fox equation $1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where T_{g1}, T_{g2}, W_1 and W_2 are the glass transition temperatures and weight fractions of polymer 1 and polymer 2, respectively, is widely used to describe the dependence of the glass transition temperature for miscible blends on composition. However, both negative and positive deviations from the equation are commonly found for many different kinds of system. Usually, for systems with strong specific interactions between the constituents, blending leads to a glass transition temperature higher than that calculated using the Fox equation[20-26]. For example, in the blends of poly(4-hydroxyl styrene) and poly(*N*,*N*-dimethyl acrylamide)[20] with strong intercomponent hydrogen bonding, for the middle compositions, the T_g of the blends is 50°C higher than the calculated weight average. In the present system, complexation between 6.9Ni-S-SEBS and STVP is obviously responsible for the unusual T_g increase.

An interesting comparison is given in *Figure 10* between the T_g dependence of bulk blend and the dependence of the reduced viscosity on the relative amount of the components. Surprisingly, the two groups of data show quite similar variations and, in particular, they peak at almost the same 6.9Cu-S-SEBS/MVP composition of around 80/20. This correlation between the results obtained from solutions and bulk is of great significance. It proves that complexation between the molecules of the ionomer and copolymer, which occurs in very dilute solution, may progressively strengthen as the solution concentration increases, and can be preserved in the final dried blend films.

CONCLUSIONS

The viscosity measurements for a series of blend solutions composed of one of the SEBS-based block ionomers with different counterions and respective counterparts, i.e. STVP or MVP, over the entire range of blend compositions at a fixed total concentration of 1% show an obvious increase in the reduced viscosity over the expected values from additivity. This behaviour reflects the formation of a complex between the polymer components. Among the counterions of the alkali, alkaline earth and transition metals studied, the transition metals, notably nickel and copper, present the greatest viscosity increase as a result of having the greatest capability for forming complex. The blends having the respective counterparts STVP and MVP show similar behaviour.

DLS studies provide more evidence of the complexation between the block ionomers and SVP. The block ionomer 6.9Ni-S-SEBS shows a bimodal distribution for R_h, associated with single chains and aggregates, respectively. For the blend solutions, both peaks apparently shift to higher values. This indicates that the single chains and aggregates of the ionomer form complexes with SVP. The polymer blends cast from THF possess much higher T_g values than the expected values from the Fox equation. The peak in the plot of T_g *versus* composition is located at ionomer/MVP 80/20, the same as that in the plot of solution viscosity *versus* composition. This correlation between the results obtained in solution and bulk suggests that complexation occurring

Table 3 T_g of the hard phase of blends of nickel or copper ionomers and MVP

	Blend					
	0/100	20/80	40/60	60/40	80/20	100/0
6.9Ni-S-SEBS/MVP T_g (°C)	90	90	108	120	118	90
6.9Cu-S-SEBS/MVP T_g (°C)	90	97	104	116	121	91

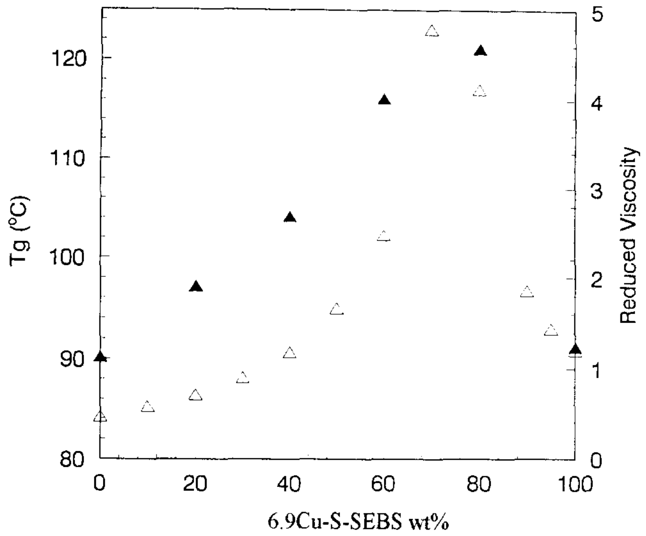

Figure 10 T_g (▲) of the hard phase of the blends composed of 6.9Cu-S-SEBS and MVP and the reduced viscosity (△) of the blend solutions in THF as a function of blend composition

in dilute solution may strengthen in the solvent-casting process and can be preserved in the final blends.

ACKNOWLEDGEMENTS

This work is part of the 'National Basic Research Project—Macromolecular Condensed State' and is also supported by the National Natural Science Foundation of China (NNSFC) and the Doctoral Programme Foundation of Institution High Education.

REFERENCES

1 Jiang, M., Liu, W., Wu, C. and Woo, K. 2nd Korea China Bilateral Polymer Symposium, Seoul, Korea, p. 53 1995
2 Jiang, M., Lui, W., Wu, C. and Woo, K. 4th Pacific Polymer Conference, Hawaii, 1995, p. 373
3 Liu W. MSc Thesis, Fudan University, 1994
4 Peiffer, D., Duvdevani, I., Agawal, P. and Lundberg, R. *J. Polym. Sci., Polym. Lett. Ed.* 1986, **24**, 581
5 Lundberg, R., Phillips, R. and Peiffer, D. *J. Polym. Sci., Polym. Phys. Ed.* 1989, **27**, 245
6 Lu, X. and Weiss, R. *Macromolecules* 1991, **24**, 5763
7 Cook, R., King, H., Jr and Peiffer, D. *Macromolecules* 1992, **25**, 629
8 Bakeev, K. and MacKnight, W. J. *Macromolecules* 1991, **24**, 4575
9 Wang, J., Peiffer, D., Shuely, W. and Chu, B. *Macromolecules* 1991, **24**, 4349
10 Agnew, N. *J. Polym. Sci., Chem. Ed.* 1976, **14**, 2819
11 Belfiore, L., Graham, H., Veda, E. and Wang, Y. *Polym. Int.* 1992, **28**, 81
12 Jiang, M., Zhou, C. and Zhang, Z. *Polym. Bull.* 1993, **30**, 449
13 Jiang, M., Zhou, C. and Zhang, Z. *Polym. Bull.* 1993, **30**, 455
14 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1982, **45**, 1
15 Qiu, X. and Jiang, M. *Polymer*, 1995, **36**, 3601
16 Qiu, X. and Jiang, M. *Polymer* 1994, **35**, 5084
17 Jiang, M., Qiu, X., Qin, W. and Fei, L. *Macromolecules* 1995, **28**, 730
18 Tucker, P. S., Barlow, J. and Paul, D. R. *Macromolecules* 1988, **21**, 2794
19 Lu, X. and Weiss, R. *Macromolecules* 1993, **26**, 3615
20 Suzuki, T., Pearce, E. M. and Kwei, T. K. *Polymer* 1992, **33**, 198
21 Wang, L. F., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci., Polym. Phys. Ed.* 1991, **29**, 619
22 Natansohn, A. and Simmons, A. *Macromolecules* 1989, **22**, 4426
23 Simmons, A. and Natansohn, A. *Macromolecules* 1990, **23**, 5127
24 Pugh, C. and Percec, V. *Macromolecules* 1986, **19**, 65
25 Yang, T., Pearce, E., Kwei, T. and Yang, N. *Macromolecules* 1989, **22**, 1813
26 de Meftahi, M. V. and Frechet, J. M. *Polymer* 1988, **29**, 477