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Compatibilization in ionomer blends

2. Coordinate complexation and proton transfer

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Summary

Copolymers of poly(styrene-co-4-vinylpyridine) (SVp) and poly(butyl methacrylate-co-4-vinylpyridine) (BmaVp) containing common minor units of pyridine were prepared. The blends of BmaVp/SVp were reacted with a series of metal acetates and carboxylic acids respectively. Due to coordination complexation between the Vp units and metal-ions and proton-transfer from the acids to Vp units, in both cases the two component ionomers carry positive charge. DSC examination of the two kinds of blends show an apparent miscibility enhancement by introducing the ion groups although there is no favorable columbic interaction between the component ionomers. These results provide a new evidence of compatibilization in the blends of the ionomers with an identical charge.

Introduction

As regard to compatibilization effect in polymer blends via introducing ion-ion interaction, differing from the most of publications in literature, this series of studies interests in the blends of ionomers with an identical charge, i.e. both component polymers carry the same, positive or negative charge. Obviously, in this case there is no columbic interaction favorable for mixing existing between the components. In the previous communication of this works[1], it was reported that in the blends of the ionomers, both of which carry a small amount of negatively charged $-COO^-$ groups, an apparent compatibilization can be observed. In this communication, this concept is extended to the blends of ionomers containing a minor component units of pyridine rings which become positively charged via coordinate complexation with metal ions and proton transfer with organic acids.

The coordinate complexation between pyridine-ring and some salts of transition metals has been known for the years, for example, vinyl pyridine can form crystalline complex with $ZnCl_2$[2], and polyvinyl pyridine form complex with some of chlorides of d-metals[3]. This complexation has also been used in blend studies, e.g. Register et al.[4] reported compatibilization in the blends of polybutadiene with carboxylic copper end-ions and copolymer of styrene and vinyl pyridine(SVp), and in blends of transition-metal neutralized sulfonated ethylene-propylene-diene elastomers (S-EPDM) and SVp[5,6]. It is noticed that in all the blends reported, the two components carry ligands (pyridine groups) and metal ions respectively, so the coordinate complexation between pyridine and metal ions results in mixing of the two polymer main chains.

Being part of our research dealing with compatibilization in the blends of identically-charged ionomers, in this work , the common units of pyridine (11.8%) in the two component polymers, i.e. copolymers of styrene and 4-vinyl pyridine (SVp) and butyl methacrylate and 4-vinyl pyridine (BmaVp), play the role of ligands. The question put forward here is whether there is compatibilization by establishing complexation between the pyridine ligands of both the components and metal ions when the blends are treated with metal salts?

As regards to compatibilization promoted by proton-transfer, there have been extensive studies in the literature[7]. The blends studied usually contain two component polymers having carboxylic acid or sulfonic acid groups and pyridine groups, respectively, so the proton transfer results in two ionomers carrying opposite charges. However, in this paper, both of the component copolymers, i.e. SVp and BmaVp having 11.8mol% of Vp units, will carry positive charge due to proton transfer from some organic acids added to the blends.

Experimental

Polymerization Monomers, i.e. Styrene (S), butyl methacrylate (Bma) and 4-vinylpyridine (Vp) were distilled, and initiator Azo-bis-isobutyronitrile (AIBN) was recrystallized. The copolymers of BmaVp and SVp were prepared by free radical copolymerization in tetrahydrofuran (THF) at 70°C using AIBN as an initiator. The polymerization was stopped at a conversion about 20-40% by pouring the reaction mixtures of BmaVp and SVp into petroleum ether and absolute ethanol respectively followed by a routine drying procedure. The pyridine contents in both BmaVp and SVp are 11.8mol% measured by nitrogen-content analysis.

Preparation of Ionomers and the related Blends The procedures for preparing solvent-casting films, powdery blends of the copolymers, and blends of the ionomers are similar with those described in the previous paper[1]. The mould films are prepared by heat-pressing the powdery mixture between two iron plates at 140°C for 1 or 10 hours.

Characterization The procedures for infrared spectroscopy, DSC and TEM are the same as described previously[1]. RuO_4 was used to selectively stain SVp component in the blends.

Results and Discussion

Compatibilization based on coordinate complexation The DSC results of the solvent-casting blend films from THF/Methanol of $SVp-Zn^{2+}/BmaVp-Zn^{2+}$ (w/w 50/50) are shown in Fig.1. The common feature of the curves is the presence of both low temperature and high temperature glass transitions associated with $BmaVp-Zn^{2+}$-rich and $SVp-Zn^{2+}$-rich phase respectively. This indicates that the blends are multiphase systems. However, there is clear variation of the Tgs with Zn^{2+} ion content, i.e. as the ion content increases, the low-Tg slightly shifts to higher temperature and

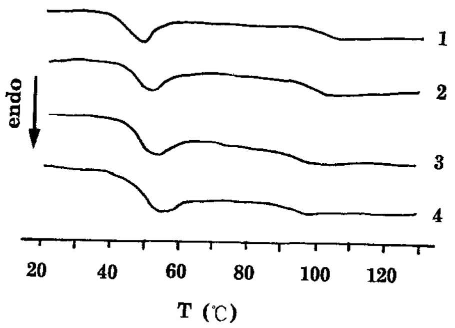

Fig.1 DSC curves of blends of SVp and BmaVp (w/w 50/50) with different contents of Zn^{2+} (film formed in methanol/THF) Zn^{2+} mol% based on Vp units: 1, 0; 2, 7.7; 3, 15.4; 4,38.4

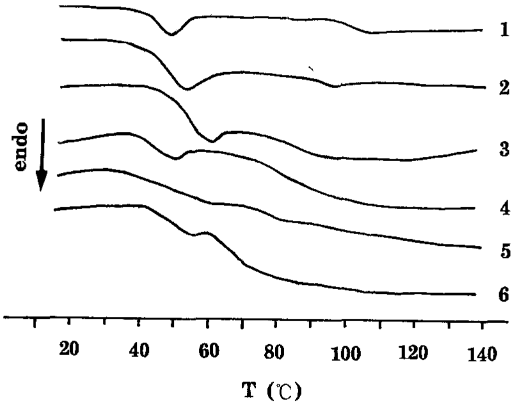

Fig.2 DSC curves of blends of SVp and BmaVp (w/w 50/50) with different metal-ions formed in methanol/THF. Metal ion mol% (The contents of the ions are shown based on Vp units): 1, 0; 2, Zn^{2+} 38.4; 3, Cu^{2+} 38.4; 4, Mn^{2+} 38.4; 5, Co^{2+} 38.4. 6, Zn^{2+} 38.4 (formed in toluene)

The high Tg shifts to low temperature apparently, this is a clear indication of compatibilization caused by the addition of the metal ions.

This compatibilization is further verified for the cases of Mn^{2+}, Co^{2+} and Cu^{2+} being used as the coordinated ions(Fig.2). all the ions show a certain ability of enhancing the compatibility as evidenced by the apparent decrease of the high Tg. This ability is in a sequence of $Co^{2+} > Mn^{2+} > Cu^{2+} > Zn^{2+}$. In the case of Co^{2+} the high Tg decreases to about 75°C , making a 25°C difference from the blend without metal ions. Considering the ion content here is only about 4.6mol% based on the total units in the main chain this compatibilization effect caused by introducing transition metal ions is substantial. In addition, the effect of solvent used in casting can be seen in Fig.2. i.e. the films cast from toluene show even strong compatibilization than those from the mixed solvent of THF and methanol.

In comparison with the results for solvent-cast films discussed above, the corresponding blends mould at 140°C present quite different behavior i.e. there is almost no difference between the Tgs of the ionomers in pure state and in the blends, which indicates a complete phase separation. TEM observation presents

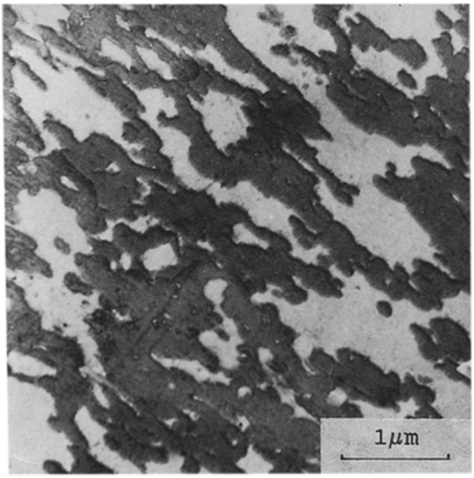

Fig.3 Electron micrograph of SVp-Zn^{2+}/BmaVp-Zn^{2+} (w/w 50/50) (the film formed by the 1 hr heat-pressing followed by staining with RuO_4)

a feature of phase separation shown in Fig.3, in which both the dark SVp-rich phase and bright BmaVp-rich phase are continuous but there is sharp boundary between them. As a general rule, the specific interactions between polymers usually diminish as temperature increases, therefore, that the mould blends show complete phase separation while solvent-cast films formed at room temperature presents apparent compatibilization is understandable. The driving force of the compatibilization observed in the solvent-cast films comes from, in our opinion, repulsion between the ion groups and hydrocarbon chain, which causes both intra-component and inter-component ion aggregation.

The coordinate complexation between pyridine and metal ions is confirmed by the infra-red studies as shown in Fig.4. It is noticed that as the content of Zn^{2+} and Cu^{2+} increases, a shoulder or a new peak appears at $1617cm^{-1}$, which can be assigned as the stretching band of C-N of pyridine ring coordinated with metal ions[8]. Quite recently, based on ^{13}C NMR studies Belfiore et. al.[8] reported that in mixtures of polyvinyl pyridine with Zinc acetate, one Zinc ion forms metal-ligand bounds with two pyridine rings when the polymer is in excess. This result presents a strong support to own augment about the compatibilization in the blends of similarly-charged ionomers[1]. In fact, it is reasonable to think that in the solution of SVp and BmaVp for solvent casting, there is a sufficient chance for a metal ion to form coordinate bonds with two pyridine groups which belong to a SVp chain and a BmaVp chain respectively, as shown schematically in Fig.6. Obviously, compatibilization is a natural consequence of this kind of coordinate complexation.

Compatibilization based on proton-transfer For studying compatibilization in the blends of ionomers formed by proton transfer, the parent copolymers used are the same as those discussed above, i.e. BmaVp and SVp with minor (11.8mol%) component Vp. The blends of the two copolymers were treated with different kinds of organic acids including oxalic acid, butanedionic acid, benzoic acid and disodium ethylene diamine (NaEDTA). The proton-transfer makes the two component polymers

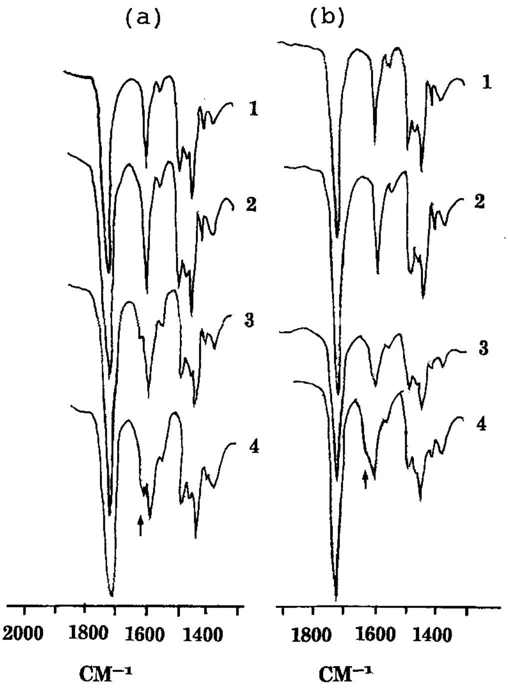

Fig.4 IR spectra of SVp /BmaVp with different metal ion contents, ion contents are calculated based on Vp units: (a) Zn^{2+}mol%: 1, 0; 2, 7.7; 3, 15.4; 4, 38.4; (b) Cu^{2+}mol%: 1, 0; 2, 3.8; 3, 14.4; 4, 38.4.

possess the common positive pyridinium groups. This reaction is evidenced by the results of IR studies, i.e. after being treated with the acids, no carboxyl stretching of the acids at about 1500cm^{-1} is detected but both the asymmetric stretching band (~1570cm^{-1}) and symmetric stretching band (1410cm^{-1}) of ionic $-COO^-$ groups appear.

The DSC curves of the solvent-cast blends of BmaVp/SVp 50/50 reacted with different amounts of oxalic acids show that the two Tgs of the two phases shift inwards as the content of the oxalic acid increases. When the content of the oxalic acid increases to 4.5mol% related to the total monomer units of the polymers, the high Tg decreases from 100°C to 85°C. This result clearly shows compatibilization in the blends of the ionomers with identical positive pyridinium.

Fig.6 presents a comparison of the compatibilization effect caused by the different organic acids. It is clear that all the acids may cause compatibilization as evidenced by the apparent decrease of the high-temperature glass transition. The ability of causing the compatibility enhancement is in a sequence of benzoic acid > oxalic acid > butanedionic acid > disodium EDTA For the case of benzoic acid, the Tg of SVp-rich phase decreases from 100°C to 75°C showing substantial compatibilization.

It is noteworthy that although there are many reports in the literature describing the compatibility enhancement in the blends of ionomers based on the proton-transfer, for all the blends the two polymer components actually carry positive and negative groups respectively. The compatibilization result reported here

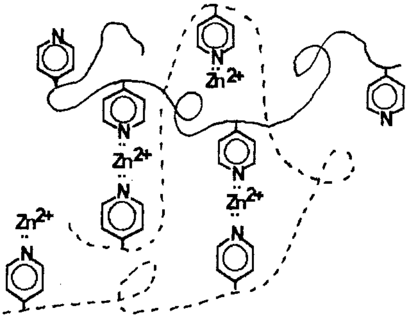

Fig.5 A schematic representation of coordinate complexation in a blend of the ionomers having common pyridine units.

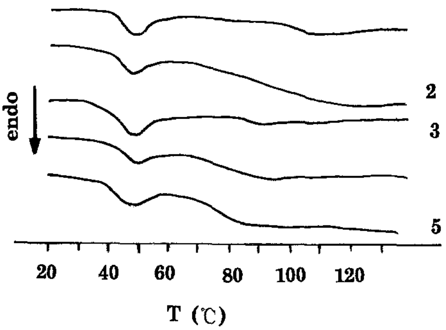

Fig.6 DSC curves of the solvent-cast films of SVp/BmaVp (w/w 50/50) with different organic acids in mol% based on Vp units: 1, 0; 2, NaEDTA 38.4; 3, Butanedionic acid 38.4; 4, Oxalic acid 38.4; 5, benzoic acid 38.4.

for the blends of ionomers with identical positive charge formed by proton-transfer from the organic acids is quite new, and obviously, this is caused by quite different mechanism, since in the present case, no favorable columbic interaction for mixing exists between the polymer components.

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