Compatibilization in ionomer blends

1. Ionomers with identical charge

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Summary
Two kinds of copolymers, i.e. poly(styrene-co-methacrylic acid) (SMaa) and poly(butyl methacrylate-co-methacrylic acid) (BmaMaa) containing a common but minor (10-20%) component of methacrylic acid, were synthesized. The blends of the corresponding ionomers of SMaa and BmaMaa neutralized with a series of metal-ions produced by solvent casting and moulding were examined by DSC and TEM. It has been shown that introducing metal-ions to the blends of copolymers apparently improves the miscibility. This miscibility enhancement depends on the nature and amount of the counter ions. In the case of SMaa-Na+/BmaMaa-Na⁺ even a single-phase blend can be produced. The results confirm compatibilization in the blends of similar-charged ionomers.

Introduction
Introduction of polar or ion groups capable of forming specific interaction into an immiscible polymer pair can improve its miscibility[1]. The ion-ion interaction in ionomer blends has been studied intensively by Eisenberg etc. [2-6]. In these studies, it is proved that two polymers of a blend containing opposite charges show apparently miscibility improvement, and in some cases introducing a small amount of ionic groups can make immiscible blends miscible. Apparently, this miscibility enhancement can be attributed to the columbic interaction between the ions with opposite charges being carried by the two component polymers, respectively. In this communication we are interested in whether the compatibilization effect still exists in blends of ionomers with identical charge. Almost no experimental information related to this question can be found in literature except that for blends of sodium-neutralized copolymers of styrene-methacrylic acid and ethyl acrylate-acrylic acid [7,8], no apparent miscibility enhancement was reported.

Experimental
Polymerization Styrene (S), butyl methacrylate (Bma) and methacrylic acid (Maa) were distilled before use. Azobisisobutyronitrile (AIBN) was recrystallized. The copolymers of SMaa and BmaMaa were prepared by copolymerization of the corresponding monomers in toluene at 70°C initiated by AIBN under a nitrogen atmosphere. The polymerization was stopped at about 30-50% conversion of the monomers by pouring the reaction mixture
into methanol/water (v/v 1/10) followed by a routine drying procedure. The compositions of the copolymers were determined by acid-base titration in methanol/toluene (v/v 1/4). In this work, SMaa with 13.7mol% of Maa and BmaMaa with 20.2mol% of Maa were used.

**Blends of the copolymers** The mixture of the copolymers was dissolved in methanol/THF (v/v, 1/4) to a 5% solution with stirring for an hour. For making solvent-casting films, a portion of the solution was transferred into a sample cell made of polytetrafluoroethylene (PTFE). The cell was loosely covered by a glass sheet for a slow evaporation of the solvent. The film samples formed over a week and were then completely dried under vacuum. For making melt molding blends, a portion of the solution was precipitated in methanol/water mixture. The dried blend powder was then moulded at about 180°C under a pressure of 6 MN/m².

**Blends of ionomers** The copolymers or their mixtures were partially neutralized with different metal acetates in methanol/THF (v/v 1/4) at 45°C for 24 hours. The reaction mixture was precipitated in methanol/water. The amount of the counter-ion was calculated based on the total molar number of Maa units. After repeating washing with methanol/water, the precipitate was press-moulded or redissolved in methanol/THF for making mould films and solvent casting films, respectively. The preparation conditions of the blend films were the same as those for the copolymer blends described above.

**Characterization** Differential Scanning Calorimetry (DSC) measurements were performed using a Dupont 1090B thermal Analyzer with a heating rate of 20°C/min under nitrogen atmosphere. The glass transition temperature (Tg) was taken as the midpoint of the abrupt heat-capacity jump between the liquid and glassy states. For transmission electron microscope (TEM) observations, the films were ultratomed first. The ultra-thin sections were then stained with vapor of 1% ruthenium tetroxide (RuO₄) solution in water for three hours and then was observed using a Hitachi H500H transmission electron microscope. Since there are no carbon-carbon double bonds in any of the components of the blends, the routine staining agent (OsO₄) was not effective. Ruthenium tetroxide (RuO₄), which had been proved powerful to selectively stain phenyl ring-containing component, was successfully used in this work to stain copolymers of styrene and methacrylic acid.

**Results and Discussion**

The Glass transition behavior of the solvent-cast films of the ionomer blends with a composition of SMaa/BmaMaa 50/50 but different sodium-ion contents covering a range from 0mol% to 52.7mol%, calculated based on the total molar content of methacrylic acid in the blends, was examined by DSC and the related results are shown in Fig.1. For the blend of copolymers SMaa and BmaMaa, without neutralization, the DSC curve clearly shows two glass transitions around 55°C and 85°C, associated with BmaMaa-rich and SMaa-rich phases, respectively. This two-phase structure does not change when a small amount (5.3mol%) of