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Counterion dependent crystallization kinetics in blends of a perfluorosulfonate ionomer with poly(vinylidene fluoride)

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Abstract

Blends of poly(vinylidene fluoride) (PVDF) with a perfluorosulfonate ionomer, Nafion®, have been prepared and examined in terms of the crystallization kinetics of the PVDF component. In blends of PVDF with Na^+-form Nafion®, the rates of bulk crystallization, as observed by DSC, and the spherulitic growth rates of the PVDF component, as observed using optical microscopy, were found to be very similar to that of pure PVDF. This behavior was attributed to the course phase separation of Na^+-form Nafion® from PVDF and melt incompatibility of the physically cross-linked ionomer with the crystallizable component. In this segregated state, the PVDF component of the blend is allowed to crystallize in pure phases that are isolated under the influence of Nafion®. In contrast, when the ionomer was exchanged with more weakly interacting quaternary alkylammonium counterions, a decrease in both the rate of bulk crystallization and spherulitic growth was observed. Furthermore, the crystallization kinetics of PVDF in these blends was found to be dependent on the counterion size; as the size of counterions associated with the Nafion® component increased, the rate of crystallization decreased. This behavior was attributed to a weakening of the electrostatic interactions in the ionomer phase and thus an increase in the extent of phase mixing with the larger ions.

Keywords: Crystallization kinetics; Nafion/PVDF blends; Counterion dependence

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer that possesses a strong electric dipole moment associated with the C–F bonds in its monomer units; and consequently, PVDF is capable of interacting with a variety of polar polymers via dipole–dipole interactions [1–13]. In an attempt to utilize the tendency of PVDF to interact with polar polymers, several blend compatibility studies have been reported for blends of PVDF with a variety of ion-containing polymers [14]. Moussaif et al. investigated the miscibility of PVDF with poly(methyl methacrylate-*co*-zinc acrylate) ionomers [15] and polycarbonate grafted with poly(methyl methacrylate-*co*-zinc acrylate) [16]. These studies showed an increasing tendency toward miscibility with an increase in the ionic functionality of the ionomer. Linares et al. [17] showed that blends of PVDF and sulfonated polystyrene have improved compatibility and mechanical stability relative to control blends containing unmodified polystyrene. In a study directly relevant to this investigation, Kyu and Yang examined the phase behavior in blends of PVDF and Nafion® in the acid and sodium neutralized forms using small-angle laser light scattering (SALLS) [18,19]. These studies demonstrated that PVDF/Nafion® blends were partially compatible below the crystalline melting point of the PVDF component; however, liquid–liquid phase separation occurred when the blends were heated above the PVDF melting point.

In a more recent study involving the morphological characterization of PVDF in blends with a perfluorosulfonate ionomer (Nafion®) [20], we found that the nature of the Nafion® counterion can significantly affect the extent of phase separation of PVDF in this blend system. Using optical microscopic and scattering techniques, blends of Na^+-form Nafion® with PVDF were shown to exhibit a large degree of phase separation, which was attributed to the strong electrostatic forces

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involved within the ionic aggregates of the Nafion® ionomer. At temperatures above the melting point of PVDF, irreversible phase separation was observed. In these blends, the ionic aggregates act as electrostatic cross-links in the Nafion® rich phase thereby reducing the mobility of the ionomer chains and hindering the phase mixing with the PVDF component. However, when the Nafion® counterions in the blend with PVDF were exchanged from the strongly interacting Na^+ cations to larger alkylammonium counterions, i.e., tetrabutylammonium (TBA^+), a weakening of the electrostatic network allowed for a greater degree of phase mixing. At temperatures above the T_m of PVDF, the blend was found to be homogeneous and characteristic of a melt-miscible system.

For a polymer blend containing a crystallizable component, the extent of phase mixing can profoundly affect the crystallization behavior. Martuscelli has demonstrated that the rate of crystallization of semi-crystalline polymers in blends is greatly affected by the extent of phase mixing of the dispersed component [21]. In general, miscible polymer blends (i.e., where the polymer chains are mixed on a molecular level) will show the greatest decrease in the rate of crystallization due to a dilution of crystalline polymer at the crystal growth front and/or an increase in the glass transition temperature of the blend. The increase in the T_g of the blend is associated with a decrease in chain mobility near the crystallites, which hinders the diffusion of crystallizable segments to the crystal growth front, thereby reducing the rate of crystallization.

In blend systems which are not miscible on the molecular level (i.e., immiscible) and exhibit some degree of phase separation, Martuscelli has shown that the crystallization kinetics of the crystallizable component is dependent on the size of the dispersed domains [21]. In highly immiscible blends which exhibit strong phase separation (i.e., large phase-separated domains), the crystallizable component can crystallize in a manner virtually independent of the second blend component and no significant reduction in the rate of crystallization is observed relative to the pure homopolymer. Conversely, in blends containing dispersed domains that are small relative to the size scale of the developing crystalline domains, the growing crystals may reject, occlude and/or deform the phase-separated domains. This behavior generally reduces the crystal growth rate of the crystallizable component to a degree correlated with the size of the dispersed domain.

Based on our previous investigations on PVDF/Nafion® blends [20], the choice of counterion type may be used to control phase mixing and thus affect the crystallization kinetics of the PVDF component. In this study, we compare the phase behavior and crystallization kinetics of PVDF/Nafion® blends containing alkali metal ions to systems containing a series of alkylammonium ions of increasing size. By changing the counterion type and systematically varying the counterion size, the extent of phase mixing in these blends may be controlled by altering the electrostatic interactions in the Nafion® component. With a variety of blend morphologies at elevated temperatures (i.e., suitable crystallization temperatures for PVDF), ranging from a system with large-scale phase separation to a homogeneous, melt-miscible state, the influence of phase mixing on the crystallization kinetics of PVDF may be evaluated.

2. Experimental section

2.1. Materials

Poly(vinylidene fluoride) (Kynar® 720, $M_w = 140{,}000$ g/mol) was obtained from Atofina. Nafion® 117 (1100 equivalent weight, sulfonic acid form) was provided by E.I. DuPont de Nemours & Co. Alkylammonium hydroxides and sodium hydroxide were obtained from Aldrich Chemical Co. and used without further purification. All other solvents and reagents were obtained from Aldrich Chemical Co. and used without further purification.

2.2. Preparation of Nafion®/PVDF blends

Soluble powders of Na^+-, tetramethylammonium (TMA^+)-, tetraethylammonium (TEA^+)-, tetrapropylammonium (TPA^+)- and tetrabutylammonium (TBA^+)-neutralized Nafion® were prepared using previously described techniques [22]. The as-received, acid-form Nafion® membranes were refluxed in an 8 M methanolic sulfuric acid solution for 1 h to ensure complete conversion of the films to the acid neutralized form. The films were then washed several times in boiling water to remove excess acid. To convert the Nafion® membranes to the neutralized forms, the acid-form films were refluxed in a 1 M solution of the appropriate sodium or alkylammonium hydroxide in 50/50 methanol/water for 1 h. The resulting films were washed several times in boiling water and dried in a vacuum oven for 24 h at 80 °C. Gravimetric analysis confirmed that this neutralization procedure resulted in Nafion® membranes with greater than 95% neutralization of the sulfonic acid groups.

Using a Parr reactor [23], the neutralized Nafion® membranes were dissolved at 250 °C and ca. 1400 psi in a 50/50 ethanol/water solution for the Na^+-, TMA^+- and TEA^+-neutralized ionomer and in a 45/5/50 ethanol/2-propanol/water solution for the TPA^+- and TBA^+-neutralized ionomer sample. Two separate procedures were utilized to recover the perfluorosulfonate ionomers (PFSIs) from solution. The TPA^+- and TBA^+-form Nafion® samples were recovered by a "steam-stripping" process [22]. The solutions were slowly dripped into a large volume of boiling water, causing the organic solvents to rapidly evaporate, leaving a white, fluffy residue of the hydrophobic ionomer. The TPA^+ and TBA^+-form Nafion® residues were recovered, dried in a vacuum oven for 24 h at 80 °C and ground into a fine powder using a mortar and pestle. The Na^+-, TMA^+- and TEA^+-form Nafion® samples were recovered from solution by slowly evaporating the ionomer solutions at room temperature under a nitrogen purge. The ionomer residues were removed from the glass evaporation dish, dried in a vacuum oven at 80 °C for 24 h and ground into a powder using a mortar and pestle. Using these two techniques, all of the neutralized forms of Nafion® were amorphous and readily soluble in solvents such as dimethyl sulfoxide.