Miscibility Studies of Perfluorinated Nafion Ionomer and Poly(vinylidene fluoride) Blends

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ABSTRACT: Miscibility studies of perfluorinated Nafion ionomer and poly(vinylidene fluoride) (PVDF) blends were undertaken by means of differential scanning calorimetry (DSC), dielectric relaxation, optical microscopy, and laser light scattering. The influence of solvent casting on the phase morphology of the blends has been examined. The spherulitic crystalline morphology of PVDF shows a strong dependence on the casting temperature and blend compositions. Solvent casting from dimethylformamide, dimethylacetamide, or 1-methyl-2-pyrrolidinone has resulted in the formation of mixed α- and γ-form crystals in a manner dependent on the casting temperature. The DSC technique is not sensitive enough for the determination of glass transition temperatures of the ionomer blends. The melting point depression of PVDF occurs but is very small. Dielectric studies show the movement of the α-transition peak, suggestive of miscible character in the solid state. However, liquid–liquid phase separation takes place above the crystal melting temperature of PVDF.

Introduction

Perfluorinated ionomer membranes have been the subject of recent interest because of their permselectivity to countercations and ion-transport properties.[1] These ionomer membranes are derived from copolymers of tetrafluoroethylene and a perfluorovinyl ether terminated by a sulfonic acid group and commercially known as Nafion.[2,3] The sulfonic acid group can be neutralized with various alkali bases or salts to form metal sulfonates. Despite the presence of bulky long side groups, tetrafluoroethylene backbone chains have the ability to crystallize.[4] The crystallinity depends on the equivalent weight of the materials.[5] Furthermore, the ionic regions are microphase separated from the matrix and often known as ionic clusters. The structure of the ionic clusters is of crucial importance, as ion transport occurs through these regions. It is, therefore, natural to witness numerous studies[6–16] on the ionic structure and ion-transport properties.

A shortcoming of Nafion in the chloroalkali cell operation is the excessive swelling,[17] thereby resulting in costly replacement of the membranes. To circumvent such problems, Nafion membranes have been used with the aid of Teflon grids. The idea that is developed is to blend Nafion with an appropriate fluorocarbon-based matrix and subsequently allow the blends to phase separate during solvent casting or by thermal treatment. The ion-transport properties of Nafion may thus be maintained through the phase-separated Nafion regions, while the materials strength in the strong electrolyte solutions would be sustained through the support of the nonionic matrix.

In the present study, we select poly(vinylidene fluoride) (PVDF) as the matrix because of the availability of abundant information in the literature with regards to its crystalline morphology, chemical and thermal stability, and other properties.[18–21] One advantage of this choice is that the material's strength can further be improved through crystallization of PVDF. We report the effect of solvent casting conditions on the phase morphology of the blends and the miscibility between Nafion and PVDF.

Experimental Section

The materials used in this study were Nafion membranes (N-117, Du Pont) with an equivalent weight of 1100 and PVDF (KF-1000, Kureha Chemical Industry Co.) with an average molecular weight $M_w \sim 282\,000$ ($M_w/M_n \sim 1.8$). Prior to blending, the Nafion membrane was cut into tiny pieces and dried at 60 °C in a vacuum oven for 48 h. Nafion and PVDF were dissolved separately by rigorous stirring at 120 °C and at room temperature, respectively, in three kinds of mutual solvents, namely, dimethylacetamide (DMA), dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP). The solutions were subsequently mixed at 1 wt % polymer concentration in various blend proportions. Blend specimens were cast on microscope glass slides at 60 °C in an air oven. The average thickness of the specimens was adjusted to about 10 μm for optical microscopy and small-angle light scattering (SALS) studies. Thicker films (approximately 70 μm) were prepared for differential scanning calorimetry (DSC) and dielectric measurements.

Optical micrographs of the Nafion/PVDF blends were obtained on a Leitz microscope (Laborlux Pol-12). Light scattering pictures were photographed with a Polaroid instant camera (Land film holder, Model 545). DSC scans were obtained on a thermal analyzer (Model 9900, Du Pont) with a heating module (Model 910). Various heating rates were employed. An indium standard was utilized for temperature calibration. Dielectric relaxation experiments were conducted on a dielectric thermal analyzer (DETA, Polymer Laboratories, Inc.) at a heating rate of 4 °C/min and at 1 kHz.

Results and Discussion

Various blends of Nafion/PVDF were cast from DMA, DMF, and NMP solutions. Figure 1 shows the optical micrographs as a function of blend ratios prepared from 1 wt % DMA solution at 110 °C. The micrographs in the upper and lower rows were photographed under parallel and cross-polarization configurations, respectively. The average spherulitic size at the intermediate compositions are somewhat larger than those at extreme compositions. Another interesting feature with the solvent casting of the 40/60 or 60/40 Nafion/PVDF mixtures is the formation of the mixed PVDF spherulites. The morphology of these spherulites is similar to the α- and γ-form crystals of pure PVDF indentified by others.[18–21] Our preliminary Fourier transform infrared (FTIR) study[22] has confirmed the formation of mixed α- and γ-crystals in the Nafion/PVDF blends. As in the case of

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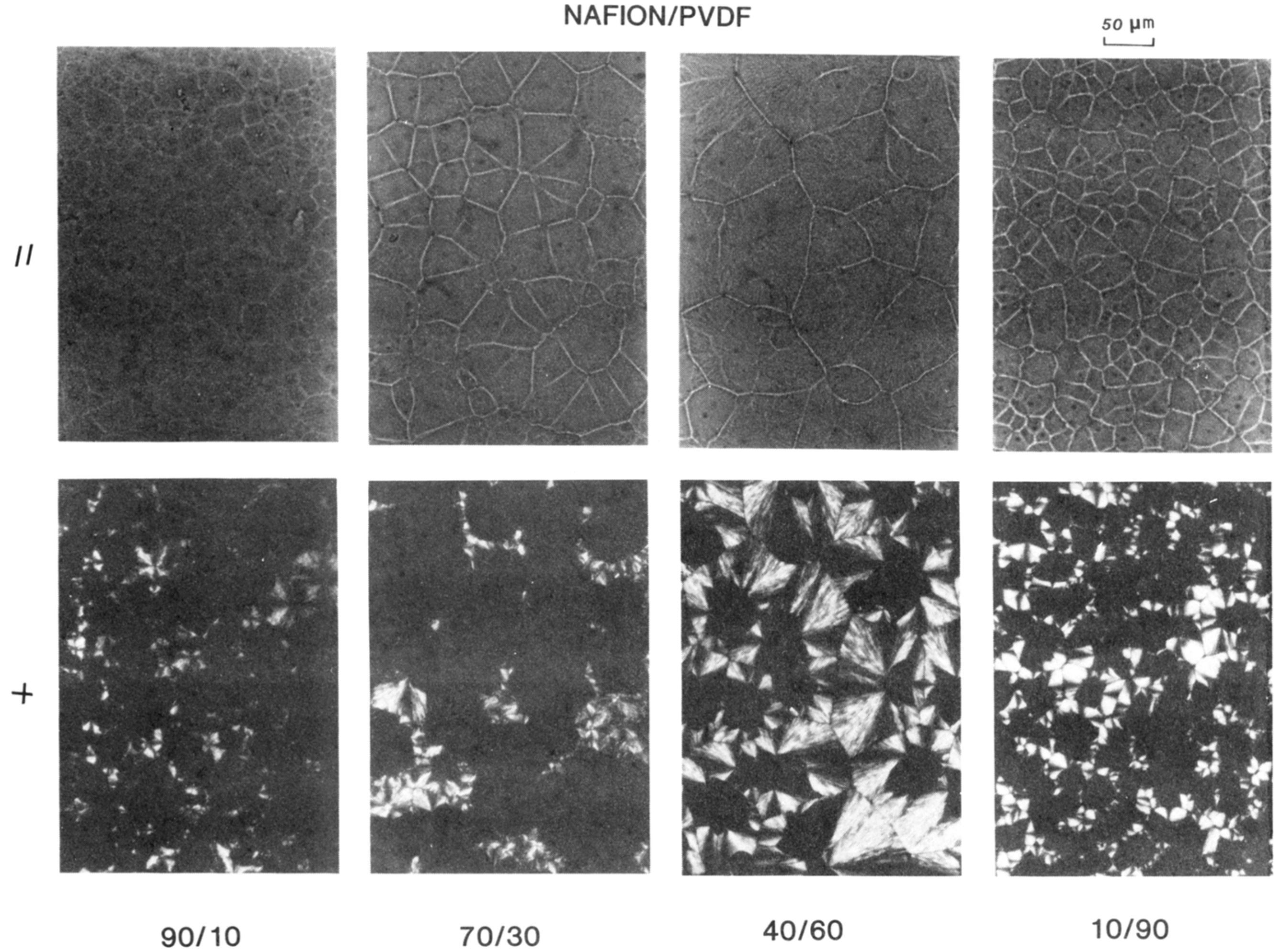

Figure 1. Optical micrographs of Nafion/PVDF as a function of blend ratios as cast from 1 wt % DMA solution at 110 °C.

pure PVDF crystallization, the α-form spherulites of PVDF in the blends with Nafion outgrow the boundaries of the γ-form spherulites. This behavior may be attributed to the differences in the rate of nucleation and crystal growth. According to Lovinger,[18,19] the nucleation rate of γ-crystals is much faster than the α-form, but the crystal growth rate is slower. As a result, the γ-form spherulites form first; then the α-form spherulites grow radially outward from the boundaries of the γ-form centers.

The size and the form of spherulites not only depend on blend compositions but are also a function of solvent casting temperature. The temperature dependence of the morphology of the 40/60 Nafion/PVDF mixture is shown in Figure 2. As pointed out previously, casting at elevated temperatures of 110–140 °C gives the large spherulites of the γ-form outgrown by the α-form crystals. When the blend is cast at 150 °C, the α-form spherulites develop predominantly. On the other hand, the γ-form spherulites are favored at low casting temperatures of 90 and 70 °C. The appearance of α- and γ-forms at high (150 °C) and low casting temperatures (70 °C) has been further confirmed in our FTIR study.[22] The above γ-form spherulites are comparatively small. At 50 °C or lower, the size of spherulites decreases further and they are difficult to see under cross polarizers.

In the case of DMF solutions, the formation of the blend morphology is similar to that of DMA solutions; i.e., mixed γ- and α-form spherulites develop at intermediate compositions of 70/30 or 40/60 Nafion/PVDF. The solvent casting from the DMF solution also shows a morphological dependence on the casting temperatures. While the mixed γ- and α-form spherulites form at 110 °C, the α-form crystals predominantly develop at higher temperatures of 150 °C. With decreasing temperature below 70 °C, the average spherulitic size decreases and becomes too small to be seen on a polarized microscope. In the case of solvent casting from NMP solutions, a similar observation was also made; thus it is not elaborated further.

For the light scattering studies, the blend films were cast at 60 °C from NMP solutions to give appropriate spherulite sizes so that the change of spherulitic patterns during melting and crystallization can be monitored conveniently. Figure 3 shows the variation of the H_v (horizontal polarizer with vertical analyzer) and V_v (vertical polarizer with vertical analyzer) scattering patterns during heating of the 50/50 Nafion/PVDF blend. The H_v scattering shows a typical four-lobe pattern characteristic of spherulite structure. The V_v scattering reveals a diffused scattering halo, reflecting the average periodicity of isolated PVDF spherulites.[23] The pattern becomes slightly brighter when the blend is heated to 150 °C; then the scattered intensity diminishes with continued heating and completely fades away at around 185 °C. The virtual increase of the scattered intensity near 150 °C may be a consequence of the annealing effect. Upon cooling from 200 °C, the four-lobe H_v scattering reappears at around 150 °C and the pattern intensifies with decreasing temperature (Figure 4). This behavior is very typical of the crystallization of semicrystalline polymers.[21]

A similar observation was also made in the blend of 60/40 Nafion/PVDF; i.e., the PVDF crystals completely

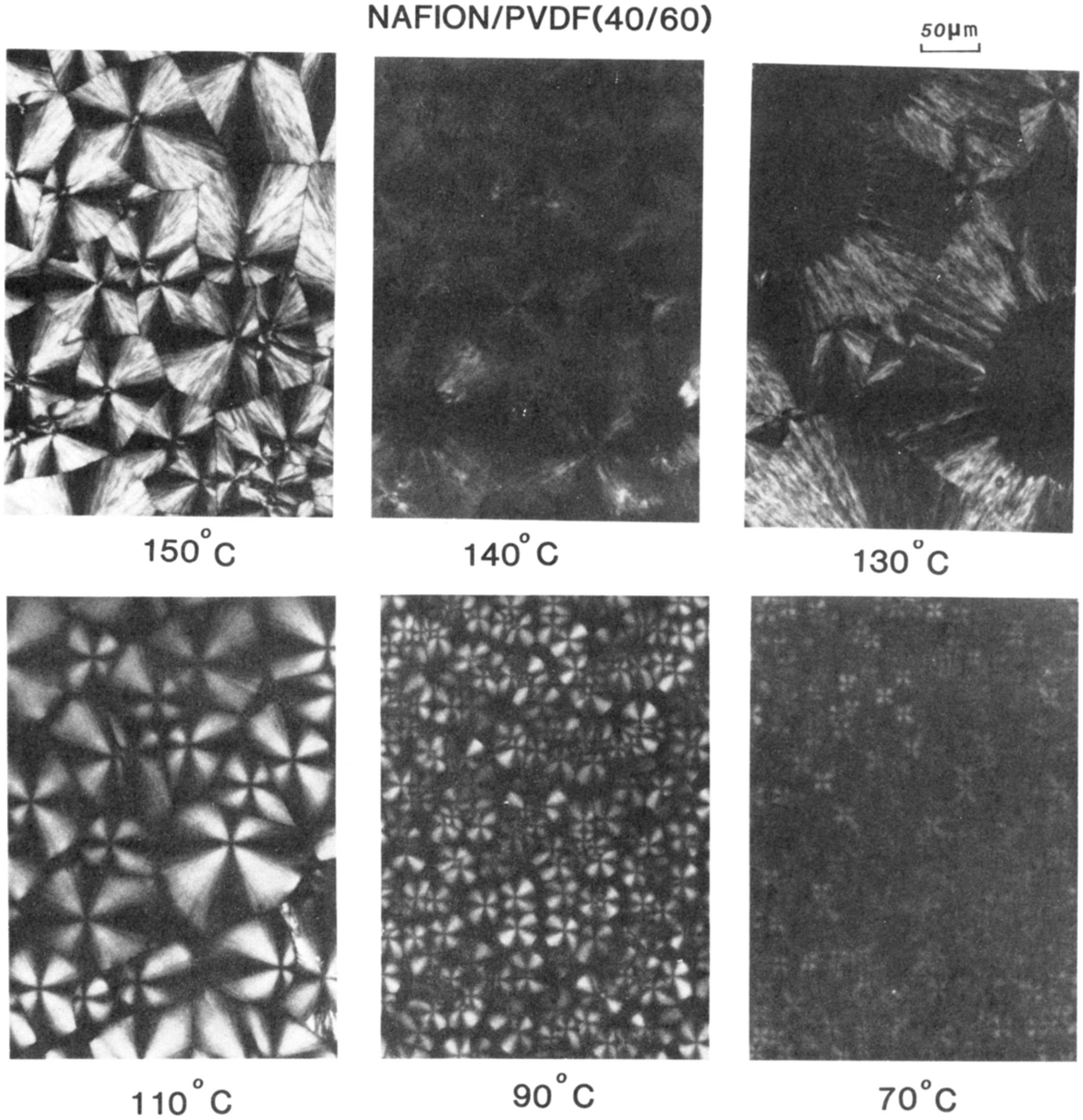

Figure 2. Temperature dependence of the blend morphology of 40/60 Nafion/PVDF.

melt at around 187 °C. Thus, the scattered intensity diminishes in the melt state. However, when the temperature increases further, a scattering halo develops at around 210 °C and gradually collapses to a smaller diameter (Figure 5). As will be shown in a subsequent paper,[24] highly interconnected domains were discerned under an optical microscope. The appearance of a SALS halo and the interconnected domains are the familiar characteristics of thermally induced phase separation by spinodal decomposition.[25,26] This suggests strongly that liquid–liquid phase separation has taken place above the crystal melting temperature of PVDF.

The presence of PVDF crystals presents some difficulty for the optical and light scattering investigations in elucidating the miscibility in the solid state. Our wide-angle X-ray result is not conclusive to identify whether or not Nafion crystals are present in their blends. The miscibility between Nafion and PVDF is therefore examined by means of DSC and DETA. DSC exotherms and endotherms for various blend compositions of Nafion/PVDF show a small but definite melting point depression as shown in Figure 6. The maximum melting endotherm (T_m) of the pure PVDF is located at around 176 °C, somewhat lower than that of the light scattering results. However, it should be remembered that the crystals do not melt completely at the peak position of the endotherm. On the other hand, the slowly melting residual crystals above the T_m can give rise to scattering of light; therefore, such discrepancy is not unexpected. When a small amount of Nafion is added to PVDF, the T_m increases slightly, which may be a consequence of enhanced nucleation. With increasing Nafion content, the melting temperature decreases, associated with the diluent (plasticization) effect. As pointed out by Wunderlich,[27] the depression of melting points can be affected by restricted crystallization in confined regions. In view of a small shift of the crystal melting points, no detail analysis has been undertaken. The melting endotherm of Nafion is not discernible in all blend compositions.

Figure 7 exhibits the storage dielectric constant and loss tangent as a function of temperature for the compression-molded PVDF. The α relaxation peak shows a strong dependence on the frequency of excitation; e.g., the tan δ peak temperature increases from 70 to 147 °C when the frequency is increased from 0.1 to 100 kHz. This peak has been attributed to crystalline relaxation. In the case of its blends with Nafion acids, the α peak moves systematically to higher temperatures with composition (Figure 8). The α dielectric peak of pure Nafion acid is located at around 180 °C at 1 kHz, which is appreciably higher than the α mechanical relaxation of 110 °C (0.2 Hz).[14,16] This may be due to the frequency effect.

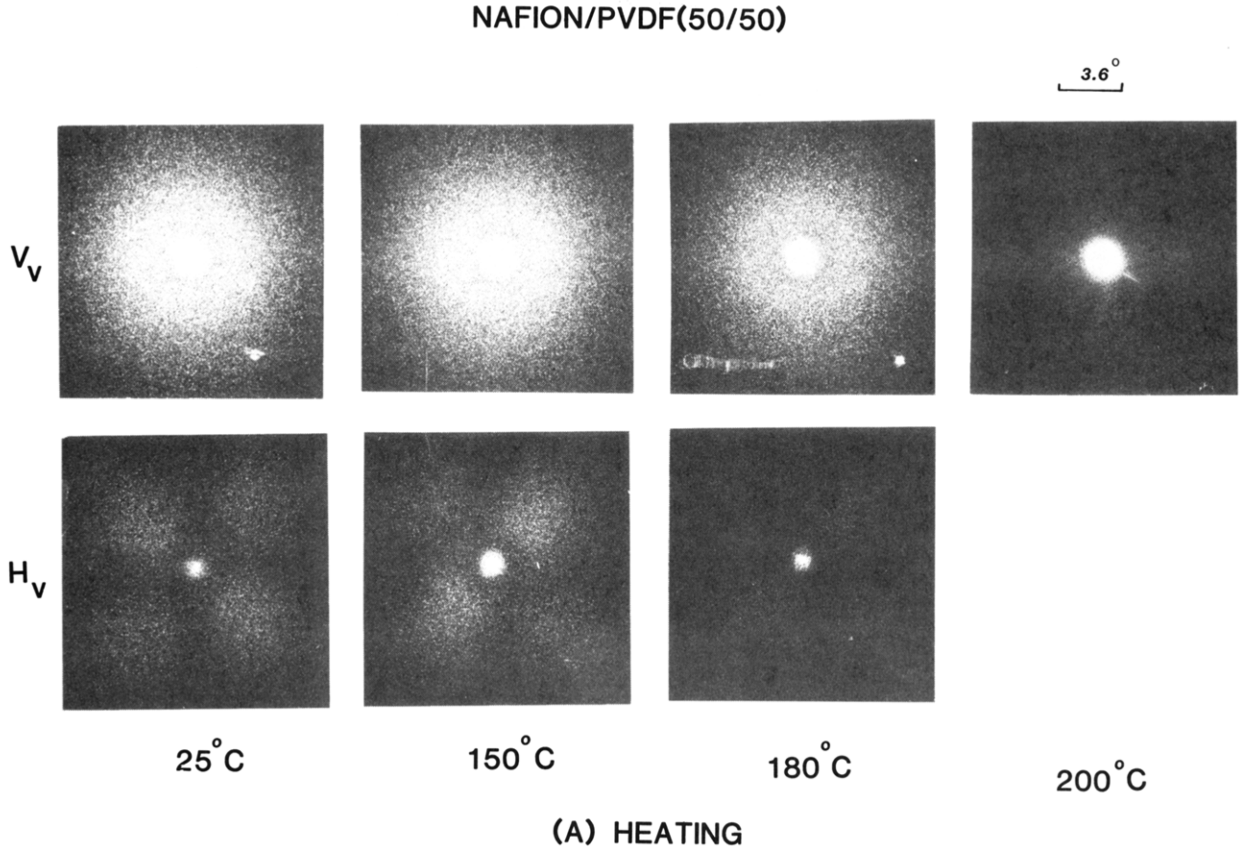

Figure 3. Variation of H_v and V_v light scattering patterns of 50/50 compositions during heating.

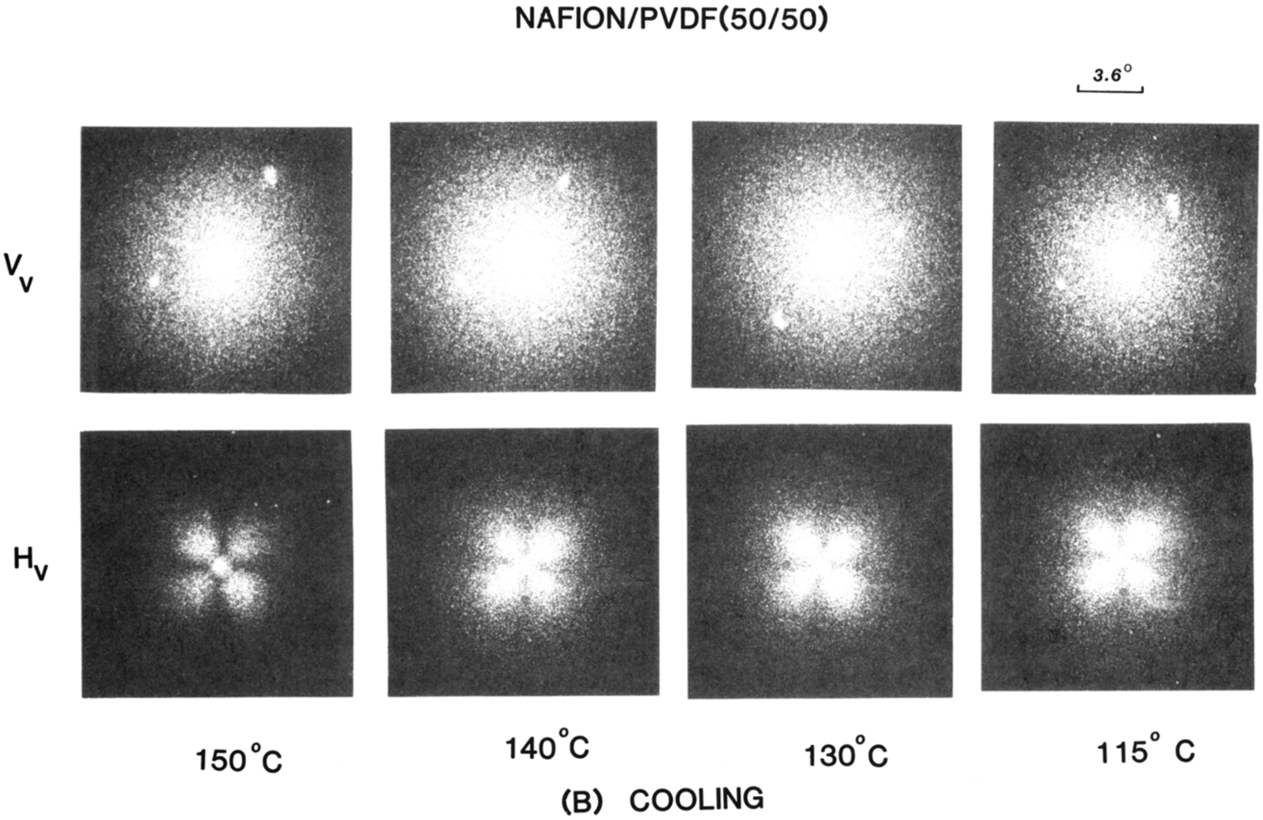

Figure 4. Change of H_v and V_v light scattering patterns of 50/50 compositions during cooling from 200 °C.

The α relaxation peak of Nafion acid has been assigned to the glass transition temperature of ion-rich regions.[14-16] The tan δ peak temperatures were further plotted against composition in Figure 9. In principle, the miscibility of polymer blends has been customarily inferred from the movement of the glass transition peaks with composition. In the literature,[28-30] the α peak of the pure PVDF was originally assigned to a crystalline origin. Hence, the movement of the dielectric α peak cannot be attributed to polymer miscibility in a straightforward manner.

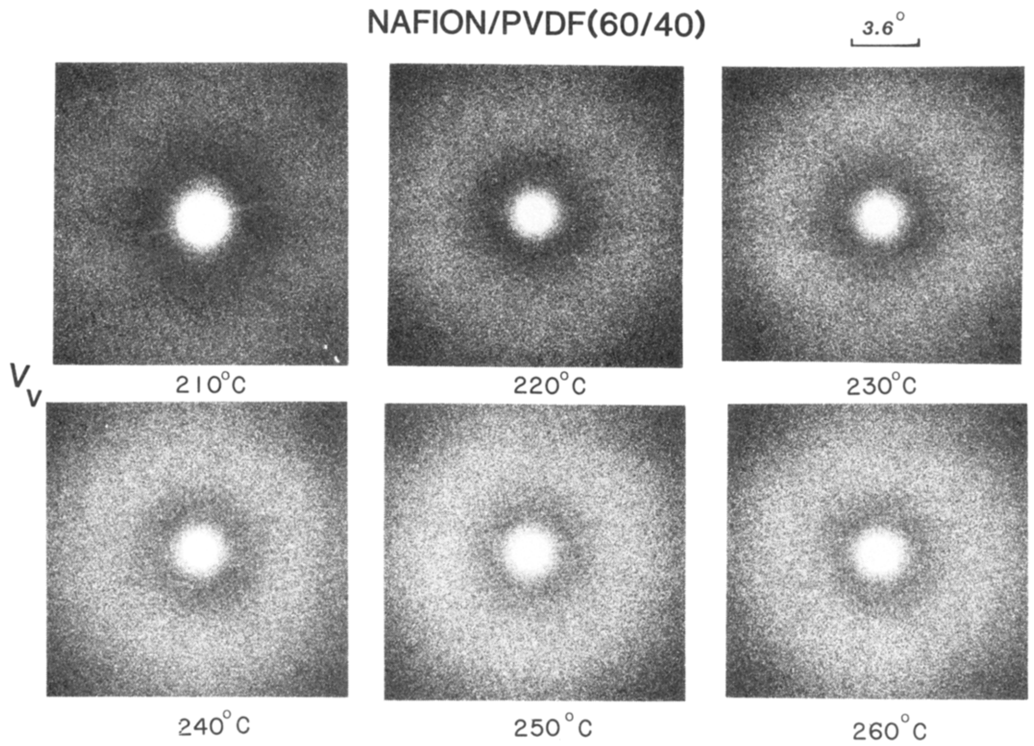

Figure 5. Evolutions of the scattering halo with temperature for the 60/40 Nafion/PVDF composition above the crystal melting temperature of PVDF.

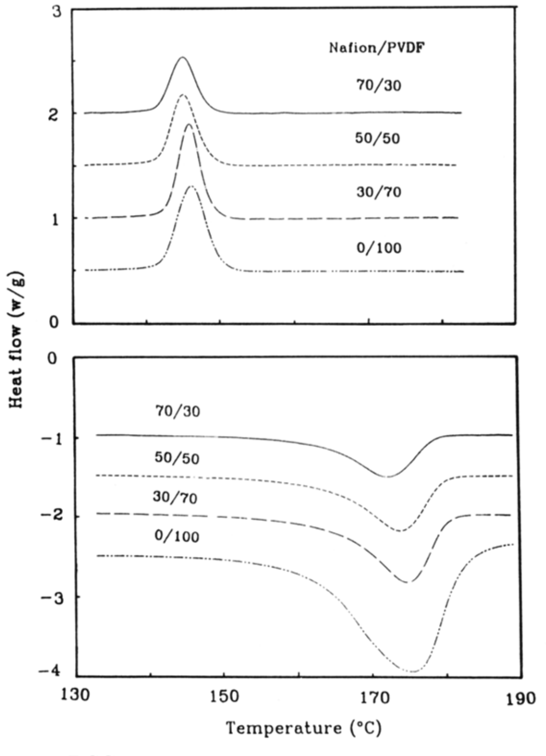

Figure 6. DSC traces for various Nafion/PVDF compositions at a rate of 10 °C/min for heating and 5 °C/min for cooling.

As pointed out by Morra and Stein,[31] the location of PMMA molecules within the preformed PVDF spherulites may be of crucial importance, i.e., whether PMMA molecules are intimately mixed with the interlamellar amorphous PVDF phase or rejected completely by the crystallizing front and pushed out to interspherulitic regions. In the former, it is likely to observe the melting point depression as well as the movement of the α crystalline relaxation peak as a function of composition. No movement is expected to be observed if the Nafion phase were completely segregated from PMMA.

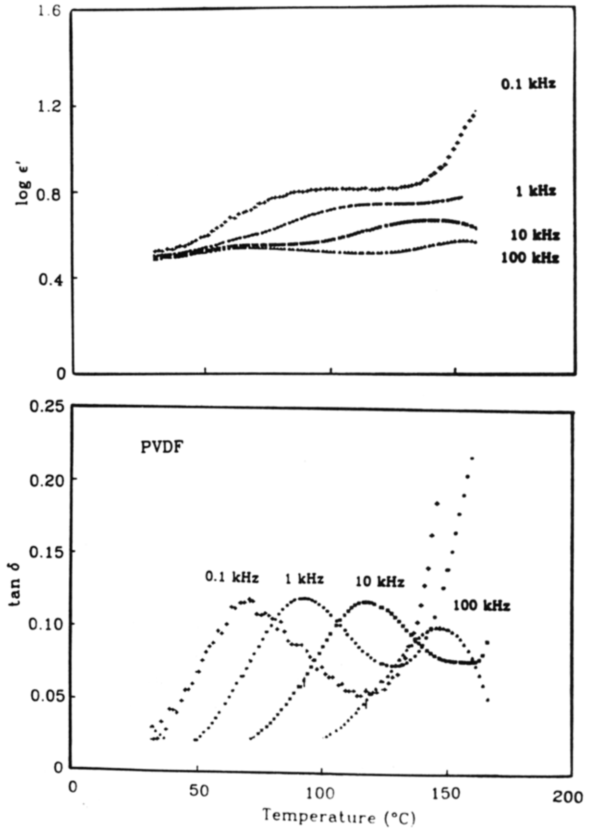

Figure 7. Storage dielectric constant and loss tangent versus temperature for pure PVDF at various frequencies.

In the present case, Nafion molecules may be in close proximity to the crystalline transition zone, presumably mixed with an interlamellar amorphous PVDF phase. Moreover, amorphous and crystalline chains do not exist in an isolated manner, but are interconnected to each other. Any perturbance from Nafion ionomers of the PVDF amorphous phase can affect its intracrystalline chain motions, thereby resulting in movement of the α

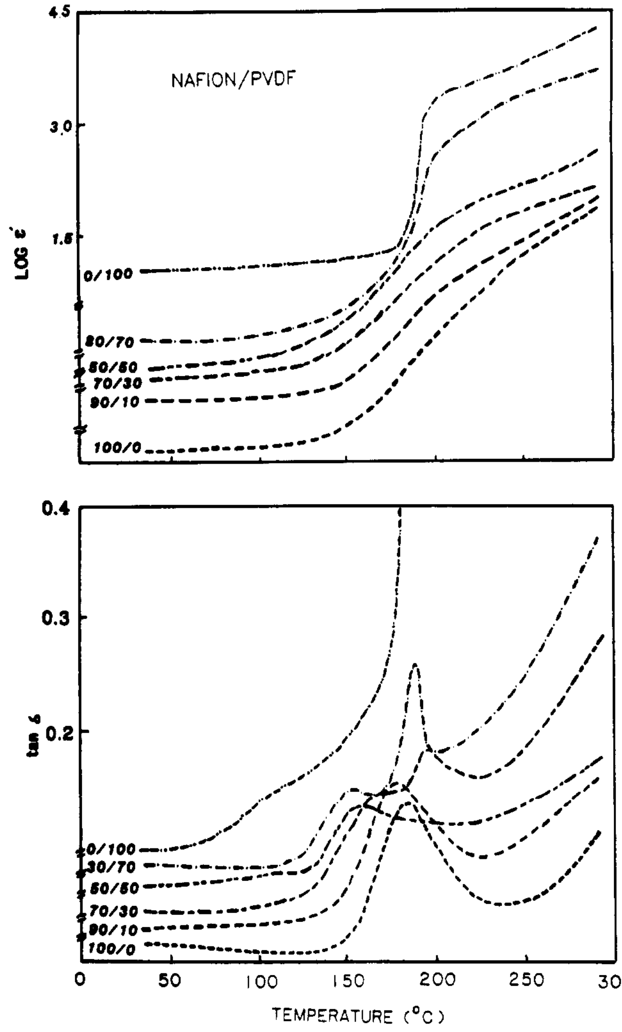

Figure 8. Storage dielectric constant and loss tangent versus temperature at 1 kHz for various Nafion/PVDF blends.

crystalline relaxation peak. This kind of compositional dependence of the α peak was also observed in the blends of PMMA/PVDF by Paul and Altamirano[29] as well as by Hirata an Kotaka[30] in their dynamic mechanical studies. The former authors expressed their concern about the assignment of the α transition of pure PVDF. In order to explain their results, i.e., the movement of the α mechanical peak with composition, the α peak of PVDF has to be identified with the amorphous phase T_g. As can be seen in Figures 7 and 8, the dielectric α peak is clearly identifiable below its T_m but disappears completely above it, indicating that the α peak may not have an amorphous origin. We thus favor the idea that the α peak of PVDF may be associated with the crystalline relaxation.

The observed miscibility or partial miscibility in blends of Nafion with fluorocarbon or hydrocarbon polymers is relatively new. Murali and Eisenberg[32] were the first to demonstrate miscibility enhancement as a result of ionic interactions in blends of functionalized poly(tetrafluoroethylene) with poly(ethyl acrylate) containing 4-vinylpyridine. The enhanced miscibility was attributed to the formation of ion pairs associated with the proton-transfer mechanism. However, the present Nafion/PVDF blend may be the first pair to exhibit partial miscibility without requiring any chemical modification.

Conclusions

We have demonstrated the effect of solvent casting on the evolution of phase structure and crystalline morphology of the Nafion/PVDF blends. The α- and γ-form crystals develop in the PVDF component during solvent casting in a manner dependent on the blend compositions and temperatures. A small melting point depression in DSC thermograms and a drastic movement of the dielectric α relaxation peak with blend composition suggest that the Nafion/PVDF may be a partially miscible pair. The mixture is unstable and undergoes thermally induced phase separation above the crystal melting temperature of PVDF.

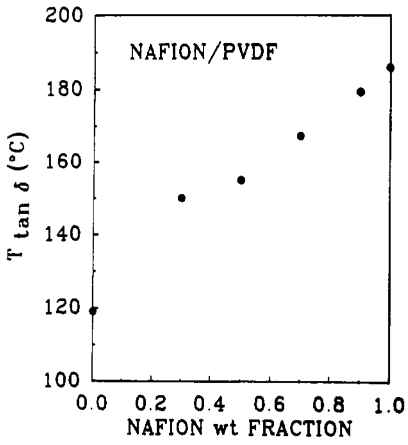

Figure 9. Variation of dielectric tan α peak as a function of blend composition.

Registry No. PVDF, 24937-79-9; Nafion N117, 119314-70-4.

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Kinetics of Phase Separation of Perfluorinated Nafion Ionomer and Poly(vinylidene fluoride) Blends

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ABSTRACT: Liquid–liquid phase separation was observed in the blends of Nafion and poly(vinylidene fluoride) (PVDF) above the crystal melting temperature of PVDF crystals. The kinetics of thermally induced phase separation in Nafion/PVDF blends was investigated by means of time-resolved small-angle light scattering. A temperature–composition phase diagram was established on the basis of cloud point measurements. The phase behavior is a lower critical solution temperature (LCST) type and reversible in character. Temperature-jump (*T*-jump) experiments were undertaken from room temperature to 220 and 240 °C. Phase separation was dominated by the late stages of spinodal decomposition. The time evolution of scattering curves was analyzed in the context of nonlinear theories and dynamic scaling laws.

Introduction

In a previous paper,[1] the effects of solvent casting on the development of spherulitic structure of poly(vinylidene fluoride) (PVDF) and the morphology of its blend with Nafion have been demonstrated. We found that the formation of α- or γ-form or mixed α- and γ-form crystals strongly depends on the temperature of solvent casting and blend compositions. The existence of a crystalline structure in the Nafion/PVDF blends makes the determination of polymer miscibility very difficult. However, the dielectric relaxation study showed a systematic movement of the α relaxation peak with composition, implying that the polymer pair may be, at least, partially miscible in the solid state. When the blend system was heated above the crystal melting temperature of PVDF, liquid–liquid phase separation took place.

In the present study, we continue our efforts to elucidate the dynamics of liquid–liquid phase separation by using time-resolved light scattering. We first establish the cloud point phase diagram. A couple of temperature jumps (*T* jumps) were carried out from room temperature to a two-phase region (220 and 240 °C) to investigate kinetics of phase separation.

Experimental Section

Nafion membranes in the acid form (N 117, equivalent weight $\cong$ 1100) were supplied by Du Pont and PVDF (KF 1000, $M_w \cong$ 282 000 and $M_w/M_n = 1.8$) was obtained from Kureha Chemical Co. They were dissolved separately in 1-methyl-2-pyrrolidinone (NMP) by rigorous stirring at 120 °C and room temperature, respectively. The solutions were subsequently mixed at 1 wt % polymer concentration in various blend compositions. Blend films were cast on microscope glass slides at 60 °C in an air oven. The average thickness of the specimens was about 10 μm.

Light scattering intensity scans were acquired on a time-resolved light scattering setup described previously.[2] A He–Ne laser (2 mW) with a wavelength of 632.8 nm was used as a light source. A set of sample hot stages was utilized for *T*-jump experiments; one is controlled at the experimental temperature and the other is used for preheating. In the present study, a second heating block was not used, as the *T*-jump experiments were carried out from room temperature to 220 and 240 °C. The scattered intensity was measured by means of a two-dimensional camera (Model 1252 B, EG & G Princeton Applied Research Co.) interfaced with an optical multichannel analyzer (OMA III, Model 1460, EG & G Co.). The data analysis, such as background subtraction, smoothing, rescaling, etc., was carried out on an off-line microcomputer (IBM-PC). Light scattering pictures were obtained by using a Polaroid instant camera (Land film holder, Model 545). Optical micrographs were photographed on a Leitz microscope (Laborlux Pol-12).

Results and Discussion

As mentioned previously,[1] thermally induced phase separation takes place during heating above the melting temperature (T_m) of PVDF crystals. Figure 1 shows a scattering halo of the 40/60 Nafion/PVDF blend at 230 °C, arising from the periodic concentration fluctuations of phase-separated domains. The optical microscopic investigation reveals interconnected domain structures, which are the familiar characteristics of spinodal decomposition (SD). SD is a spontaneous process that is extremely unstable at infinitesimal concentration fluctuations.[3,4] An alternative mechansim is nucleation and growth (NG), which is stable at small fluctuations but is unstable at large composition fluctuations. In the latter process, a stable nucleus forms first and the phase-separated domains grow subsequently. If this process were to occur, a component of scattering should decrease from a maximum at $q = 0$, which is not seen here. In other words, liquid–liquid phase separation occurs through SD rather than NG.[3,4]

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