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Structure of Styrene Grafted Poly(vinylidene fluoride) Membranes Investigated by Solid-State NMR

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ABSTRACT: The poly(vinylidene fluoride), PVDF, membranes that have been radiation grafted with polystyrene, PS, producing PVDF-*g*-PS membranes, are intermediates in the synthesis of PVDF-*g*-polystyrenesulfonic acid (PSSA) polymer electrolyte membranes. Solid-state NMR measurements were carried out to study the structure of the PVDF-*g*-PS membranes. The previous investigations by thermal methods and by X-ray scattering showed phase separation of the two polymeric components. The extent of phase separation and the mobility of the components in the membranes were investigated by NMR relaxation time measurements and by 2-D wide-line separation (WISE) experiments. It was shown that the amorphous PVDF and PS are phase separated into domains larger than several nanometers. The amorphous PVDF component also retained higher mobility than the PS. Information on the structure of the intermediate product can be used when interpreting the properties of the final polymer electrolyte membrane.

Introduction

Polymer electrolyte membranes can be used in a variety of electrochemical membrane processes. Among many other techniques, a way to produce polymer electrolyte membranes is the radiation-induced grafting of monomers into preformed polymer films followed by functionalization of the grafted component.[1−4]

The properties of the final polymer electrolyte are highly dependent on the structure and properties of the original polymer film and of the grafted polymer component.[1−7] The matrix polymer component provides the mechanical properties as the grafted polymer provides the desired functionality. In the case of polymer electrolyte membranes the control of water content, water localization, and the continuity of the hydrophilic phase are necessary in the means of an application. These properties are to some extent determined already during the grafting. Thus, the morphology of the system is important when considering the final properties of the membrane.

The irradiation-initiated grafting of styrene into PVDF film occurs mainly in the amorphous phase of PVDF, disturbing the crystalline structure of PVDF only to a minor extent.[5] It results in a complex, phase-separated structure of crystalline PVDF, amorphous PVDF, and amorphous PS. The phase separation of the components is evidenced by the loss of transparency of the PVDF film after grafting, by the changed diffraction pattern in SAXS diffractograms,[6] and by microscopic studies.[7] Information on the extent of the phase separation and on the mobilities of the two polymers is accessible via solid-state NMR studies.

^{13}C CPMAS relaxation time measurements can give information on the miscibility and local heterogeneity in composite polymer materials.[8−12] The determination of miscibility on the molecular scale is based on spin−lattice relaxation times of protons. Unless the two polymeric components have the same inherent relaxation times, they are miscible if they exhibit the same relaxation time. The determination of the size of the phase-separated structures is based on the time scale of the measurements used and on the estimation of the spin diffusion coefficient. A difference in the proton spin relaxation time $T_{1\mathrm{H}}$, which is of the order of seconds, of the two components would reveal phase-separated domains larger than tens of nanometers. A difference in the proton spin relaxation time in the rotating frame $T_{1\rho\mathrm{H}}$, typically milliseconds, of the two components means that the phase-separated domains are larger than some nanometers.

The 2-D wide-line separation (WISE) method combines the structural information from the directly detected ^{13}C dimension with the dynamical information from the indirectly detected ^{1}H dimension.[9,11,12] The mobilities of the individual PVDF and PS components can be investigated on the basis of structural information from the ^{13}C spectrum. By inserting a mixing time into the WISE pulse sequence, the size of the phase-separated domains can be estimated, based on spin diffusion as in the case with relaxation measurements.

In this paper the aim has been to study the morphology of the styrene grafted PVDF membranes by means of solid-state NMR.

Experimental Section

Materials. Membranes were prepared by the three-step method described in previous communications.[2,5] In this method a commercial PVDF membrane (Goodfellow, 80 μm) was irradiated with an electron beam, producing radical sites that initiate grafting onto the PVDF chain. The grafting of the membranes was carried out immediately after irradiation in 50/50 v/v styrene/toluene mixture for varying periods of time. Styrene (Fluka) and toluene were reagent grade and used as received. The membranes were then extracted in a Soxhlet apparatus with chloroform overnight and dried to constant weight. The degree of grafting was

$$\text{degree of grafting} = \frac{m_1 - m_0}{m_0} \times 100\% \qquad (1)$$

where m_0 is the original mass of the sample and m_1 the mass of the grafted sample.

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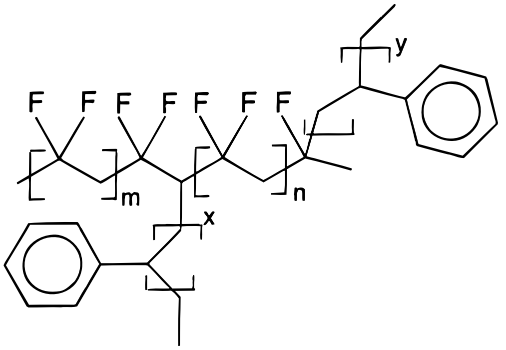

Figure 1. Tentative chemical structure of the PVDF-*g*-PS membranes.

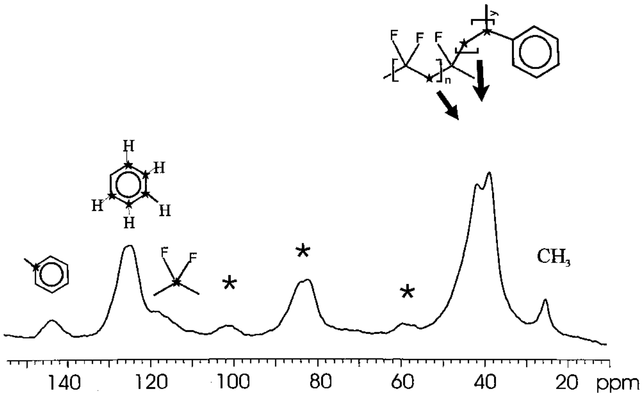

Figure 2. Solid-state ^{13}C CPMAS spectrum of PVDF-*g*-PS membrane, degree of grafting 48%. Spinning sidebands are marked with *.

^{13}C CPMAS NMR Measurements. The measurements were made with a Varian ^{UNITY}INOVA spectrometer operating at 300 MHz for protons. The spectra were obtained under matched Hartmann−Hahn conditions with a Varian CPMAS probe. For the measurements the membrane samples were rolled into 7 mm silicon nitride rotors. Proton dipolar decoupling, cross-polarization (CP), and magic angle spinning (MAS) were used in order to obtain the CPMAS spectra. In the measurements typically over 1000 transients were collected over a spectral width of 20 kHz, using a pulse delay of 3 s and pulse length of 5.5 μs for a 90° pulse. The spinning speeds used were from 3200 to 4200 Hz. A contact time of 1000 μs was used to obtain the standard CPMAS spectra of samples.

Proton T_1 relaxation, T_{1H}, was measured by the inversion recovery method. The time delay after the 180° pulse was varied from 0.02 to 6 s. To obtain the relaxation time for protons in the rotating frame, $T_{1\rho H}$, contact times from 600 to 8000 μs in the CPMAS sequence were employed.

The WISE spectra were collected at room temperature using a contact time of 500 μs, spinning speed 4200 kHz, 1024 complex data points in the ^{13}C dimension, and 64 increments in the ^{1}H dimension. Mixing times used were from 5 to 200 ms.

Results and Discussion

Solid-state NMR measurements were made on the radiation grafted PVDF-*g*-PS membranes in order to study phase separation phenomena and mobility of the components. The tentative molecular structure of the PVDF-*g*-PS membranes is presented in Figure 1. The measured ^{13}C CPMAS NMR spectra showed that the PVDF-*g*-PS membranes consist of carbons with several resonance frequencies. The assigned spectrum of the PVDF-*g*-PS membrane, degree of grafting 48%, is shown in Figure 2.

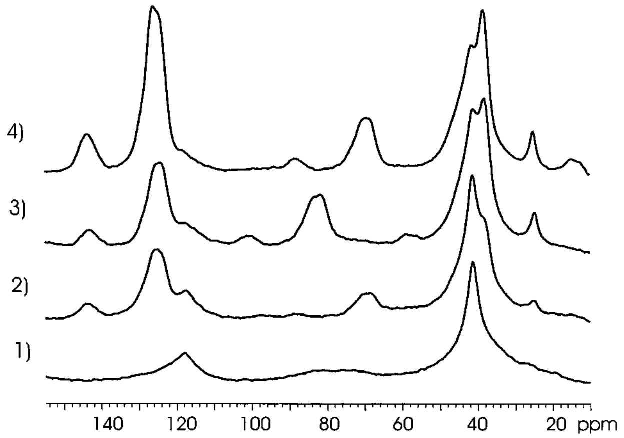

Figure 3. Solid-state ^{13}C CPMAS spectra of PVDF film and PVDF-*g*-PS membranes: (1) PVDF film, (2) PVDF-*g*-PS membrane, degree of grafting 18%, (3) 48%, and (4) 73%.

The methylene carbons of the PVDF moiety and the methylene and methine carbons of the PS backbone chains have broad resonance frequencies around 40 ppm. The intensity increase of the 38 ppm peak compared with the 41 ppm peak with increasing polystyrene content in the samples is clearly seen in Figure 3. The 41 ppm peak originates from the CH_2 carbon of the PVDF and the 38 ppm peak from the main chain carbons of the PS chain. The peak at 41 ppm was assigned to PVDF in all the relaxation time calculations, while the aliphatic backbone chain carbons at 38 ppm and aromatic carbons at 125 ppm were assigned to PS.

The methyl peak at 25 ppm was assigned to the end groups of the polystyrene chains. Due to the high intensity of the peak, it can be assumed that the number of polystyrene chains is large and that the chain length of the grafts is thus relatively small. The peak intensities in CPMAS spectra however depend largely on the experimental parameters of the measurement. This makes the estimation of the chain length of the grafts very difficult, and no numbers can be given in this report. As the graft chain length and its variation with the synthesis parameters is a very important matter, it will be further studied.

Relaxation Time Measurements. The T_{1H} results obtained for the PVDF-*g*-PS samples are presented in Figure 4a. They are almost the same for the respective carbons in the different spectra. This would show homogeneity of the matrices on the length scale of tens of nanometers. The T_{1H} of the 48% grafted PVDF-*g*-PS sample are plotted against temperature in Figure 4b. The relaxation times decrease slightly with increasing temperature, but the values are within error limits for the individual PVDF and PS components. The T_{1H} relaxation times are comparable with the values reported for PVDF in ref 13.

The $T_{1\rho H}$ relaxation times are plotted against increasing polystyrene content in Figure 5a. The values stay practically the same for the respective carbons. This indicates either true homogeneity on the length scale of few nanometers or the same inherent relaxation times for both components. In Figure 5b the $T_{1\rho H}$ relaxation times of the 48% grafted PVDF-*g*-PS sample are plotted against temperature. By increasing the temperature, the $T_{1\rho H}$ values of the PVDF and PS components separate from each other. The values for the two PS peaks show a similar temperature dependence. The temperature behavior of the PVDF relaxation times $T_{1\rho H}$

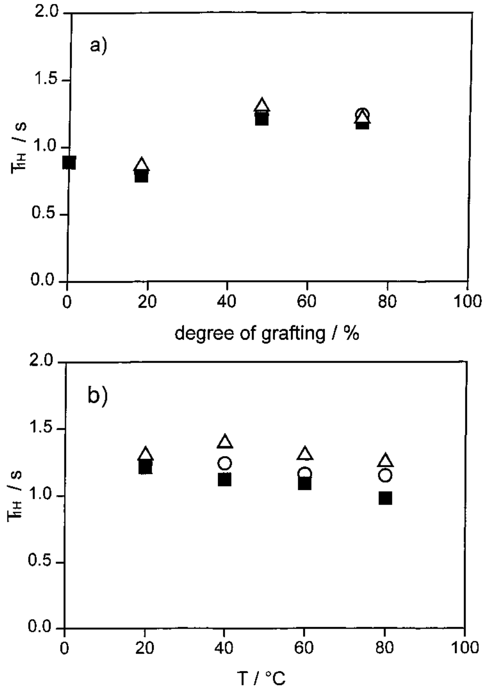

Figure 4. $T_{1\mathrm{H}}$ relaxation data of the PVDF film and PVDF-*g*-PS membranes: (■) PVDF peak at 41 ppm, (○) PS peak at 38 ppm, (△) PS peak at 125 ppm. (a) $T_{1\mathrm{H}}$ plotted against the degree of grafting; (b) $T_{1\mathrm{H}}$ of PVDF-*g*-PS membrane with degree of grafting 48% plotted against temperature.

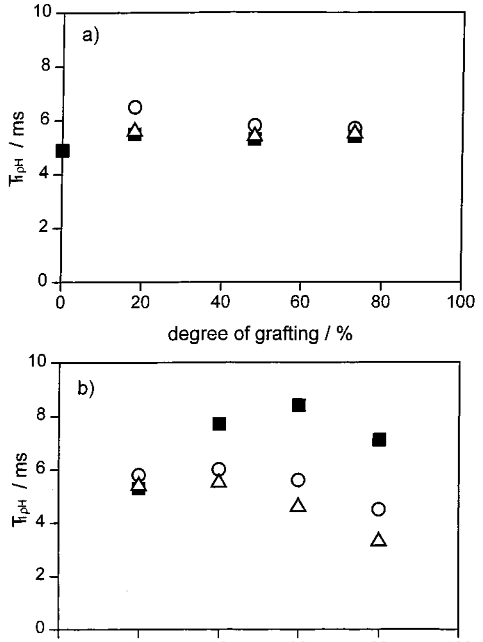

Figure 5. $T_{1\rho\mathrm{H}}$ relaxation data of the PVDF film and PVDF-*g*-PS membranes: (■) PVDF peak at 41 ppm, (○) PS peak at 38 ppm, (△) PS peak at 125 ppm. (a) $T_{1\rho\mathrm{H}}$ plotted against the degree of grafting; (b) $T_{1\rho\mathrm{H}}$ of PVDF-*g*-PS membrane with degree of grafting 48% plotted against temperature.

is similar to the results reported in ref 13. Thus, we conclude that the PVDF-*g*-PS membranes have phase-separated domains larger than a few nanometers, but smaller than some tens of nanometers.

2-D WISE Measurements. 2-D WISE spectra combine structural information from the directly detected ^{13}C dimension and information about the mobility in the indirectly detected ^{1}H dimension. The narrower the peak in the ^{1}H dimension is, the more mobile the component. The domain sizes in heterogeneous systems can be extracted by a spin diffusion experiment, i.e., inserting a mixing time into the pulse sequence, in which time the signals have time to equilibrate.

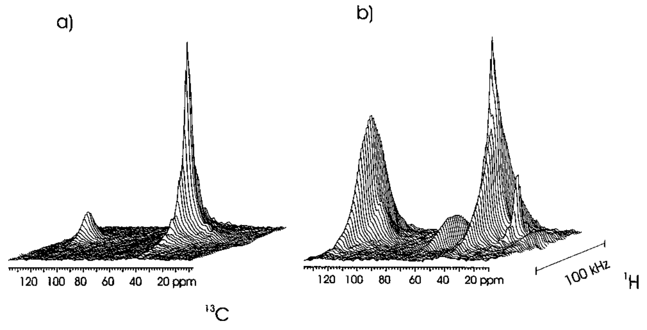

Figure 6. 2-D WISE spectra without mixing time: (a) PVDF film; (b) PVDF-*g*-PS membrane, degree of grafting 48%.

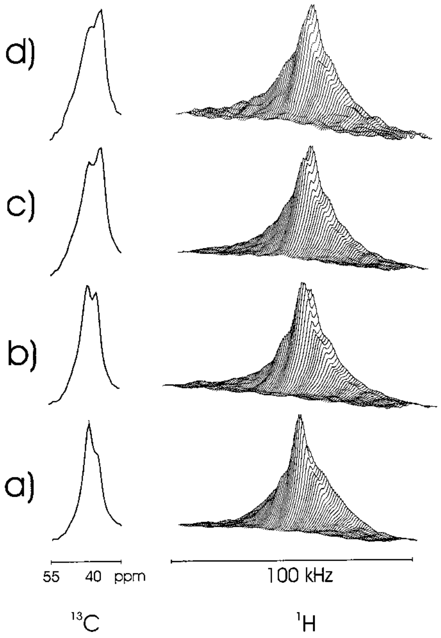

Figure 7. Slices of 2-D WISE spectra of PVDF-*g*-PS membrane, degree of grafting 48%: (a) no mixing time, (b) mixing time 5 ms, (c) mixing time 20 ms, and (d) mixing time 200 ms.

2-D WISE spectra of the PVDF film and of the PVDF-*g*-PS membrane, degree of grafting 48%, without a mixing time are shown in Figure 6. The WISE spectrum of PVDF in Figure 6a shows the intense narrow peak in the ^{1}H dimension at 41 ppm originating from the mobile amorphous phase of PVDF and the broad base of the peak due to crystalline PVDF. The WISE spectrum of the PVDF-*g*-PS membrane, where the peak at 41 ppm originating from PVDF is clearly narrower than the corresponding PS peak at 38 ppm, is shown in the Figure 6b. This demonstrates that the amorphous phase of PVDF with T_g around −40 °C is more mobile at room temperature than PS with T_g around 100 °C. Thus, the PVDF still retains most of its mobility after grafting.

Figure 7 presents slices of WISE spectra of a PVDF-*g*-PS membrane, degree of grafting 48%, measured without a mixing time and using 5, 20, and 200 ms of mixing time. As the mixing time is increased, it can be seen that the intensity of the peak originating from

PVDF decreases, and the shape of the peak in the ^{1}H dimension begins to resemble the shape of the PS peak. The equilibration of the peak intensities is already completed after 20 ms of mixing time since the spectra with 20 and 200 ms of mixing time are nearly the same.

This result is in agreement with the results from the relaxation time measurements. The 20 ms mixing time for spin temperature equilibration corresponds to a domain size of some nanometers.[12] This quantity is the shortest distance in the heterogeneities. However, the shape of the phase-separated domains is not very likely to be globular. As the grafting reaction proceeds in a preformed PVDF film, already oriented due to melt processing,[7] it is likely that the PS grafts are themselves oriented inside the matrix. Thus, we suggest that instead of a globular domain structure with PS "beads" inside the PVDF matrix, a more likely picture is that the PS grafts are somewhat oriented along the PVDF matrix. Based on the NMR studies, it is evident that some aggregation or coiling of the PS grafts occurs, explaining the nanometer scale phase separation detected in NMR.

The morphologies of the PVDF-*g*-PS and the sulfonated PVDF-*g*-PSSA membranes have also been studied by atomic force and electron microscopy and by X-ray diffraction and Raman spectroscopy studies.[7] In the atomic force microscopy scans micrometer scale blobs on the surface of the PVDF-*g*-PS membranes were observed. On the other hand, in the Raman spectroscopic measurements it was found that at a high degree of grafting, 73%, the PVDF-*g*-PS matrix was homogeneous on the scale of micrometers. The NMR investigation shows that the PVDF-*g*-PS membranes are homogeneous on the level of micrometers and that the phase separation of the matrix occurs on a nanometer scale.

Conclusions

The morphology and mobility of the components of styrene grafted PVDF films were studied by means of solid-state NMR. The ^{13}C CPMAS measurements indicated that the number of PS grafts is large and the chain length of the grafts is thus small. In the proton spin relaxation studies it was found that the PVDF and PS are phase separated into domains larger than several nanometers but smaller than some tens of nanometers. The 2-D WISE method was used to study the mobility of the components and, by inserting a mixing time in the pulse sequence, also the morphology of the membranes. It was found that the PVDF component retained its mobility after grafting and that the PS component was less mobile. The WISE method showed that the components are phase separated into domains of several nanometers. Due to the preparation technique, the shape of the PS domains is not likely globular. Thus, it is concluded that the membranes consist of aggregates or coils of PS chains inside the largely oriented PVDF matrix.

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