Preparation of Proton-Conducting Membranes by Direct Sulfonation. 1. Effect of Radicals and Radical Decay on the Sulfonation of Poly(vinyl fluoride) Films

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The effect of irradiation treatment on the structure and sulfonation reactivity of polyvinyl fluoride (PVF) films was studied mainly with EPR and IR spectroscopy. The main radical species produced by electron irradiation are aliphatic radicals, whereas proton irradiation creates a significant amount of polyenyl radicals. The half-life time of the aliphatic radicals was about 6 h. FTIR study shows that sulfonation reaction of PVF is a single-stage process and thus the formed sulfonic acid structures do not react further and produce new structures. In addition, it is independent of the irradiation treatment. Despite the careful synthesis and removal of O_2 from the sulfonation solution, the most important side reaction produced by the sulfonation is the formation of C=O functionalities. Irradiation treatment increases the C=O content. Both the sulfonation time and sulfonation reagent concentration demonstrate similar linear correlation with the extent of oxidation. Therefore, the oxidation cannot be decreased by means of optimizing these variables. The only important factor allowing adjustment of the structure of the final membranes is the type of irradiation and radical decay in the case of proton irradiation. Irradiation with either electrons or protons did not increase the ion exchange capacity as measured with a titrimetric method. IR study of the samples showed, however, indication of the formation of derivates of sulfonic acid in the proton-irradiated samples containing radicals.

Introduction

Functionalization of polymers in the solid state gains more and more attraction due to the easiness of the method in addition to the economics. In the simplest case this conversion may include only the functionalization and purification of, for example, polymer films. Thus, the necessary investments in the production lines can be low because of the few stages necessary to convert, for example, a hydrophobic polymer to a hydrophilic or an isolating polymer to a conducting matrix.

During recent years our work has been focused on the development of low-price ion conductive and ion exchange active membranes. Our method has been the direct sulfonation of partially fluorinated polymer films[1−3]

in which the initial matrix is sulfonated without any assisting synthetic routes. Commercial poly(vinyl fluoride) (PVF) has been used as a matrix polymer. The key feature of our method is the use of ionizing radiation in the manipulation of the membrane properties. Necessary ion conductivity has been reached by irradiating the original matrix with a proton beam prior to the sulfonation.[1] The increase in conductivity achieved by the proton irradiation is significant as the conductivities of such membranes have been as much as 2−5 times higher than that of the respective nonirradiated or electron beam-irradiated samples. We have shown that irradiation with protons increases also the sulfonation rate,[1] aggregation of the sulfonic acid groups,[2] and water uptake.[1−3] In addition, it has been shown that these membranes have very low dimensional changes upon hydration and dehydration but work well in low-

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temperature fuel cells.[4] However, the reaction mechanisms and factors which define the formation of such special structures and properties found in the proton-irradiated and sulfonated PVF membranes have not yet been studied in detail. In addition, the advantage of the irradiation was achieved only with rather long sulfonation times and high concentration of the sulfonation reagent. Consequently, as ion conductivity and ion exchange capacity approached the necessary level, the mechanical properties were most often deteriorated. Thus, there is need for lowering the extent of sulfonation but retaining the advantages of irradiation treatment. To do this, it is necessary to study in detail all the variables of the modification method.

A number of important properties of the sulfonated membranes can be achieved by means of irradiation treatment prior to the sulfonation. This is due to the structural changes caused by the irradiation, that is, radiolytic changes. The most important radiolytic changes with respect to the sulfonation are changes in crystallinity and average chain length of the polymer and formation of new and highly reactive functionalities.[5] The most reactive radiolysis products are radicals. If only the radicals are either mobile or otherwise reachable, they tend to react. Depending on the environment, the radicals can produce both direct and indirect effects on further functionalization like sulfonation. Direct effects are seen in the direct reactions with, for example, sulfonation reagent. Indirect effects are mainly due to such structural changes of the matrix as cross-linking, chain scission, and formation of double bonds and conjugated structures and most often also carbonyls because of the reaction with O_2.[5,6] To be able to optimize the functionalization reaction, it is thus essential to know in detail which kind of radicals are produced by the irradiation treatment as well as the decay rate of different radical species. In addition, it is essential to know the influence of the sulfonation conditions and the morphology of the original polymer matrix on the properties of the final membrane.

In this work we present the first part of a comprehensive study on the chemical and physical aspects of direct sulfonation of PVF films with the primary goal to find the ways to adjust and optimize the properties of the final materials. This part is mostly devoted to the investigation of the influence of radiolysis products on the structural changes of the host matrix, the course of sulfonation reaction, and the effect of sulfonation conditions on the material performance.

Experimental Section

Irradiation and Sulfonation. All prepared membranes were based on the commercial Tedlar PVF films produced by DuPont. As an unoriented film, Tedlar TTR10AH9 was used and the biaxially oriented film was Tedlar TTR10SG3. Both films were 25 μm thick. The samples investigated in this work were prepared mainly in a similar way to that reported earlier.[1] Briefly, the first step of preparation was irradiation. Both electron and proton beams were used to study the effect

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Table 1. Preparation of the Samples Studied and the Ion Exchange Capacity Determined

sample #	irradiation type[a]	radical decay time	acid concentration (%)[b]	sulfonation time (min)	Q (mequiv/g)
1	EB	10 min	1.5	60	0.44
2	EB	1 h	1.5	60	0.54
3	EB	5 h	1.5	60	0.39
4	EB	5 days	1.5	60	0.43
5			1.5	60	0.34
6	H+	10 min	1.5	60	0.47
7	H+	1 h	1.5	60	0.45
8	H+	5 h	1.5	60	0.35
9	H+	5 days	1.5	60	0.31
10			1.5	60	0.47
11	H+	1 h	1.5	30	0.10
12	H+	1 h	1.5	45	0.34
13	H+	1 h	1.5	60	0.45
14	H+	1 h	1.5	75	0.66
15	H+	1 h	1.0	60	0.16
16	H+	1 h	1.5	60	0.45
17	H+	1 h	2.0	60	0.84
18	H+	1 h	2.5	60	1.21

[a] EB, electron beam; H+, proton beam; adsorbed dose 400 kGy.
[b] Volume % of chlorosulfonic acid in 1,2-dichloroethane.

of the type of irradiation. Irradiation with electrons was performed with electron beam equipment CB-150 Electrocurtain (Electrosciences Inc., 175 keV). The samples were subjected to the beam eight times with a single absorbed dose of 50 kGy. With each of the irradiations the dose rate was 660 kGy/s. Proton irradiations were done with an EGP II tandem accelerator with the proton energy of 2.5 MeV. The average energy loss for protons in the films was 680 keV/ion (calculated with SRIM 98.01 code) and the total absorbed dose was 400 kGy. The dose rate was on average 600 Gy/s. During proton irradiation the PVF films were in a vacuum and during irradiation with electron beam the films were in a N_2 atmosphere. After irradiation the samples were kept in liquid N_2 until the following stage.

Sulfonation of the samples was done in N_2-bubbled 1,2-dichloroethane/chlorosulfonic acid solution for 30–85 min at RT. Both the chlorosulfonic acid (Merck) and 1,2-dichloroethane (Merck) were reagent grade. The chlorosulfonic acid content varied between 1.0 and 2.5 vol %. After sulfonation the samples were purified from soluble impurities by rinsing or extracting with pure 1,2-dichloroethane (Merck), acetone (Merck), and finally, with ion-exchanged water. Detailed specification and description of the studied samples is given in Table 1.

Radical Decay Measurements. Decay of radicals present in the irradiated films was measured with a Varian E-9 EPR spectrometer. The samples were kept in liquid N_2 until the measurements to avoid decay of the radicals. Samples were measured in plugged glass tubes flushed with N_2 prior to the plugging. The decay was studied at RT.

IR Measurements. Infrared absorption measurements were performed with a Bruker IFS-66v FTIR spectrometer, equipped with a liquid-nitrogen-cooled MCT detector. Spectral resolution was set to 2 cm^{-1}. In each measurement at least 50 single scans were collected. To study all spectral regions, the samples were investigated in two forms: equilibrated with water and heavy water, respectively. Exchange of the samples from H-form to D-form was done by drying the samples twice in a vacuum at 80 °C for 24 h. After both of these drying procedures, the samples were soaked for 3 h in a large excess of D_2O. The curve-fitting procedure was performed using PeakFit software (Jandel Scientific Corp.).

Ion Exchange Analysis and Bromination. The ion exchange capacity of the samples was measured as described elsewhere.[1] Briefly, after drying the samples in a vacuum desiccator at 70 °C for 24 h, the dry weights were determined. Thereafter, the samples were kept in NaOH solution (10 mM) for 3 days. Finally, the excess NaOH was titrated with HCl (5 mM). Cresol red was used as the indicator.

Few samples were brominated to identify the spectral features seen in the IR spectra. Bromination was done by keeping the dried samples (vacuum oven at 50 °C for 24 h) in Br_2/CCl_4 solution for 48 h at RT. During the reaction, the reaction bottles were shielded from light. After reaction, the samples were washed with pure CCl_4 and finally dried in a vacuum oven at 50 °C for 24 h.

Results and Discussion

The details of preparation of the samples studied in this work are collected in Table 1 along with the measured values of ion exchange capacity (Q). As the precision of the ion exchange analysis was only 0.10 mequiv/g, it can be concluded that the Q values are practically the same for all samples with the same sulfonation conditions and thus no effect arising from the radicals produced by the irradiation treatment could be seen. This is in accordance with our earlier results because we have noticed that irradiation increases the ion exchange capacity only with the Q values roughly over 1 mequiv/g.[1] However, it is obvious that significant differences between the samples with different irradiation treatment can be seen with more sensitive methods. Therefore, the same samples were studied in detail both with EPR and with FTIR.

1. EPR Analysis. In the following we discuss first the common features of the EPR spectra of the electron- and proton-irradiated samples. The EPR spectra are shown in Figure 1. The spectra of both samples taken a few minutes after irradiation are dominated by a somewhat asymmetric line, which exhibits significant intensity over a range of about 250 G and a hyperfine structure with a typical splitting of about 35 G. Seguchi et al. attributed similar but significantly better resolved EPR spectra in γ-irradiated samples of poly(vinylidene fluoride) to the aliphatic radical $-CH_2-CF^\bullet-CH_2-$.[7] Our density functional (DFT) computations for a series of aliphatic radicals show that fluorine nuclei both in the α-position and in the β-position to the radical center can exhibit hyperfine couplings of the observed magnitude. This is because α-fluorine nuclei are situated approximately in the nodal plane of the singly occupied molecular orbital (SOMO), while β-fluorine nuclei can be situated either in the nodal plane or significantly outside this plane depending on the conformation of the radical. For this reason we cannot assign the observed spectrum to a single radical species; rather we conclude that the comparatively poor hyperfine resolution is due to a superposition of the spectra of several types of aliphatic radicals with fluorine nuclei in the α- or β-position.

After longer decay times, the spectrum of these aliphatic radicals becomes weaker and this signal has vanished 24 h after the irradiation in both samples. The spectrum which persists after 24 h is much narrower, extending only over a range of about 75 G and significantly asymmetric. This spectrum can be explained as a superposition of the asymmetric spectrum of peroxy radicals $R-O-O^\bullet$ and the symmetric spectrum of polyenyl radicals $-(CF=CH)_n-CH^\bullet-$ with a half-width of about 30 G. In agreement with this hypothesis of a superposition of the spectra of two species, the long-
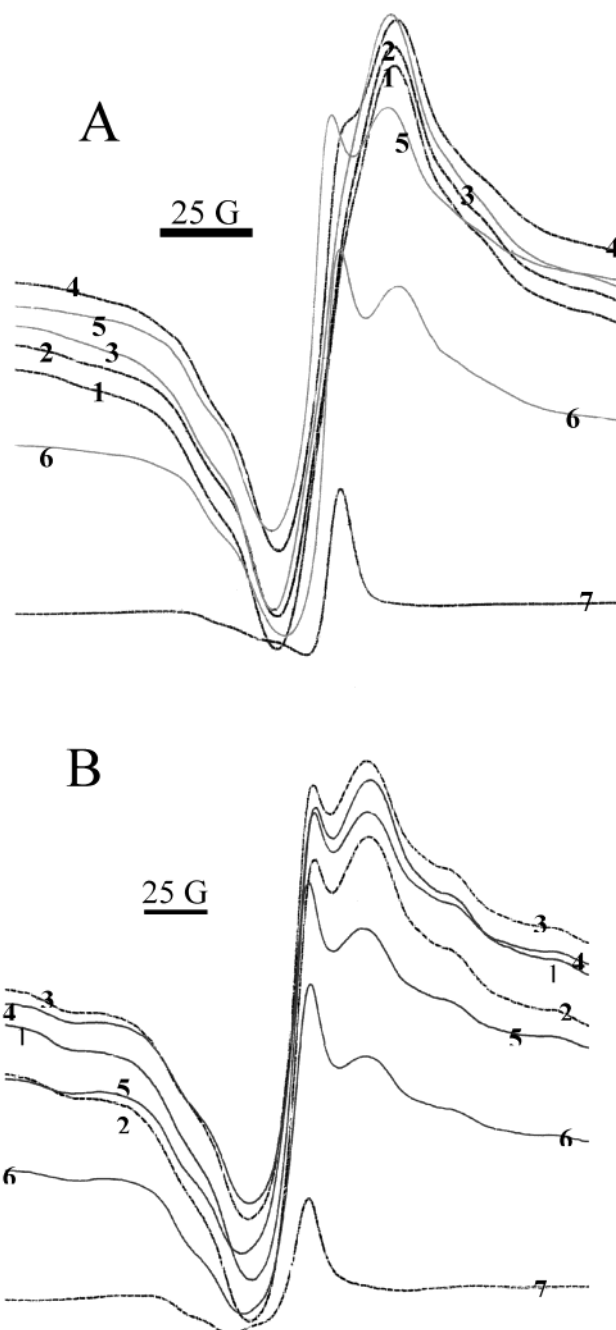

Figure 1. EPR spectra of irradiated PVF membranes measured at different times after irradiation (as indicated): (A) Electron beam-irradiated (decay times (min): 10 (1), 15 (2), 34 (3), 108 (4), 231 (5), 356 (6), and 1440 (7)); (B) Proton-irradiated (decay times (min): 10 (1), 16 (2), 38 (3), 102 (4), 225 (5), 343 (6), and 1440 (7)). Adsorbed dose is 400 kGy in both cases.

time persistent spectra are slightly different for the electron- and proton-irradiated samples. The spectra of both theses species have also been observed in γ-irradiated and heavy ion-irradiated PVDF membranes.[7,8] Komaki with coauthors[8] observed the appearance of the spectrum of polyenyl radicals after irradiation at a high ion fluence ($>10^{12}/cm^2$), but also for irradiation at a lower ion fluence after annealing for a long period at

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room temperature. Seguchi et al.[7] observed polyenyl radicals after annealing the samples for 1 week at room temperature or for 3 h at 110 °C in a vacuum. Moreover, in both studies the peroxy radicals were the dominant species after exposition of the samples to air for a few minutes. Therefore, we assume that the short exposition to air during handling can be the cause for the appearance of these radicals in our samples.

We have also investigated the decay kinetics of the aliphatic radicals by analyzing the time dependence of the spectral intensity at a field where there is virtually no contribution to the spectrum by the long-time persistent radicals (B_0 = 324.0 mT). Within experimental error, decay follows first-order kinetics with the time constant of T_H = 393 ± 15 min and T_e = 362 ± 15 min for the proton- and electron-irradiated samples, respectively. Unfortunately, it is impossible to analyze the growth kinetics of the polyenyl and peroxy radicals in the same way due to the strong overlap of the spectra. However, it is qualitatively apparent from the series of spectra, in particular for the electron-irradiated sample, that the polyenyl radicals do not already exist at their final concentration immediately after irradiation. Therefore, we conclude that the polyenyl radicals are a decay product of the aliphatic radicals, which is in agreement with the observations on PVDF by Seguchi et al. and Komaki et al.[7,8] Interestingly, the concentration of the aliphatic radicals also appears to increase for a few minutes after electron irradiation (see Figure 1B). We attribute this effect to a change of the distribution between the different types of aliphatic radicals, which may cause a change in the spectral line shape. In agreement with this conjecture the hyperfine resolution in the electron-irradiated sample slightly decreases during the first few minutes after irradiation.

Although the general behavior is very similar for the two types of irradiation, there are a few differences. First, immediately after irradiation the ratio of the concentration of the polyenyl radicals to the aliphatic radicals is significantly higher in the proton-irradiated one. This can be rationalized as the formation of polyenyl radicals requires the reaction between several primary defect centers. This is more likely in a spur with closely spaced defects as it is produced by proton irradiation where the average energy loss per angström is 2 orders of magnitude larger than for electrons. Second, the initial concentration of radicals is by a factor of about 4 larger in the electron-irradiated sample compared to the proton-irradiated sample. This is again understood by considering the higher initial local concentration of radicals with proton irradiation, which leads to a larger probability for the radicals to react to cross-links and double bonds, which are diamagnetic defects. A third difference is the significantly better hyperfine resolution in the proton-irradiated samples, which indicates a narrower distribution of aliphatic radical species. We can only give a tentative explanation of this, which is again related to the fact that proton irradiation produces a higher initial local concentration of radicals. In such a situation, the most unstable aliphatic radicals are expected to decay faster since they should be preferentially involved in the formation of cross-links and double bonds.

Taken together, the EPR results suggest the following scheme of radical formation and subsequent reactions. The dominant radical species 1 min after irradiation are aliphatic radicals with fluorine nuclei both in the α-position and in the β-position to the radical center. In addition, some polyenyl radicals are already formed, especially with proton irradiation. At the same absorbed dose of 400 kGy, the total radical concentration is by about a factor of 4 larger with electron irradiation. The aliphatic radicals present 1 min after irradiation are likely to be relatively isolated from each other. These radicals decay with a time constant of about 6−6.5 h, thereby forming new polyenyl radicals. The concentration of the polyenyl radicals after complete decay of the aliphatic radicals is much lower than the initial concentration of the aliphatic radicals themselves. This is due to the fact that the formation of one polyenyl radical with n double bonds requires $2n + 1$ aliphatic radicals, but probably also due to the fact that the dominant decay products of the aliphatic radicals are diamagnetic species (cross-links and double bonds). The polyenyl radicals, in turn, decay on a time scale of several days.

2. Evaluation of the Effect of Radicals on the Ion Exchange Capacity. To make some quantitative conclusion on the effect of the radicals on the sulfonation reaction, it would be essential to know the radical concentrations of the studied samples. Unfortunately, we did not have possibilities to measure them directly. However, some estimation can be done on the basis of literature values. The yields of different products formed upon irradiation are given as the *G*-value. Its defines the number of formed products per 100 eV of energy absorbed. In general, the *G*-values for the radical formation with different fluorinated aliphatic polymers are falling between the range of 0.2 and 5. The *G*-value depends on, for example, the type of polymer matrix, irradiation method, and the overall irradiation procedure. For PVF irradiated with γ-radiation the radical yield has been reported to be 0.22.[9] This value gives with the absorbed dose of 400 kGy radical concentration of 0.01 mmol/g in PVF. Alternatively, a *G*-value of 2 would give a radical concentration of 0.09 mmol/g. These values can further be correlated to the sulfonation yield. If we assume that no chain reactions are taking place in the sulfonation, then consequently no significant changes in the sulfonation rate are expected to be seen in the ion exchange capacity results.

3. FTIR Analysis. We have used FTIR spectroscopy to study more closely the structural differences between the prepared samples as a function of irradiation type, radical decay time, and differences in the sulfonation conditions. In the following we give the results of the extensive IR analysis of the samples.

In our previous studies we have noticed that in the IR spectra of the directly sulfonated PVF a pronounced feature appears in the spectral region of 1500−1800 cm^{-1}.[2,3] This new broad multicomponent band was independent of the amount of water in the sample, thus excluding implication of SO_3H-containing species in the formation of the spectra. Therefore, we tentatively assigned this feature to the structural changes created

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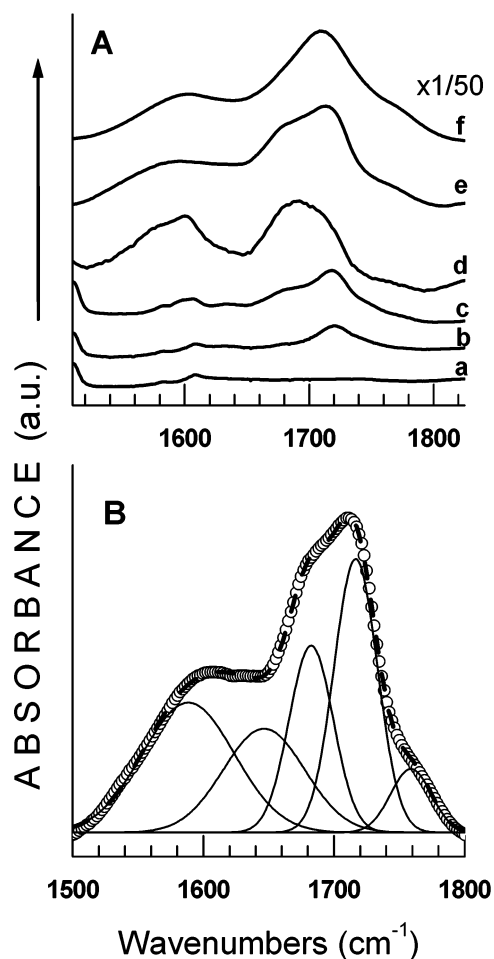
Figure 2. FTIR spectra of PVF membranes in the spectral region of structural defects. All spectra are normalized with the intensity of the band of CH_2 stretching vibrations (2850–3000 cm^{-1}) and shifted along the *Y*-axis for better comparison. Plot A: a, initial; b, proton-irradiated (dose 1 MGy); c, sulfonated in H_2SO_4 (80 min, solution at 85 °C) after proton irradiation; d, sulfonated without irradiation in $ClSO_3H$ (1.5%, 1 h, room temperature); e, same as "d", but different morphology of the matrix (sample #5 in Table 1); f, sulfonated in $ClSO_3H$ (2.5%, 70 h, room temperature). Plot B: Results of the curve fitting for directly sulfonated PVF membrane (same curve as "e" in plot A).

in the polymer structure during sulfonation. However, detailed analysis of this event has not been done yet.

Figure 2A compares infrared absorption spectra of the PVF membranes subjected to the different treatment in the spectral region of interest. It is seen that irradiation causes only minor spectral changes (compare curves a,b), resulting in appearance of a weak band at about 1720 cm^{-1}—the characteristic feature of structural changes (e.g., −C=C−) created in a polymer structure by ionizing radiation. In contrast, sulfonation gives rise to several strong new bands in the region of 1500–1820 cm^{-1} and, moreover, the observed spectral profiles depend on the variables of the sample preparation. Thus, for instance, the membrane sulfonated with concentrated H_2SO_4 at room temperature shows no spectral changes at all in the region of interest (spectrum not shown). When the sulfonation was performed at 85 °C (curve c), only minor variation of the spectrum is observed. However, these samples were mechanically unstable.

Another set of materials was prepared by sulfonating two different kinds of PVF films. With both samples the sulfonation time was 1 h and the sulfonation was done with 1.5 vol % chlorosulfonic acid solution in 1,2-dichloroethane. One PVF film was free from stress (curve d) and the other one was biaxially stretched (curve e). It is seen in Figure 2A that the spectral profiles differ significantly. This difference is explained by the difference in permeability properties of the matrixes as the film with no stress can easily swell upon sulfonation but the stretched one not as much. Consequently, as the sulfonation front proceeds closer to the middle part of the film, the membranes tend to swell. This swelling is limited, however, in the film with biaxial stretching. When the sulfonation time of the film with stress increases (curve f), spectral intensity of the absorption bands in this region rise dramatically but the general band shape remains practically unchanged. Such behavior indicates that chemical reactions between the polymer and chlorosulfonic acid are single-stage processes, and further reactions between the sulfonation agent and previously formed products do not take place. It is also important to note that despite the high intensity of the discussed bands (i.e., large extent of the structural modification), these membranes demonstrated rather good mechanical properties and were completely applicable for a fuel cell. Thus, another important conclusion can be made, namely, that observed structural changes are not related to the mechanical stability of the final material.

Figure 2B shows part of the IR absorption spectrum of the sample #5 (nonirradiated) along with the results of the curve-fitting procedure. It is seen that at least five different components centered at about 1590, 1645, 1680, 1715, and 1760 cm^{-1} can be resolved. In accordance with numerous reports[10−14] several different structures have characteristic bands in this spectral interval. At first, it is the stretching vibration of carbonyl groups (C=O) and it covers a wide frequency range (1550–1850 cm^{-1}) and most often with a very strong intensity. Other possible assignments are −C=C− species (≤1650 cm^{-1}), −CH=C=CH_2, and >C=C=CH_2 groups (1700 ± 40 cm^{-1}); the frequencies of these bands may be higher if the species contain C−F bonds.[12] We note, however, that the spectral intensity of the C=C double-bond vibrations is most often low. For example, in the case of electron- or Krypton-irradiated PVDF, the corresponding spectral features became very detectable only with an as high absorbed dose as 3 MGy.[15] To clarify the nature of the observed bands, bromination of some samples was done. A clear change in the color of the samples from black to yellow—clear evidence for the reaction of C=C bonds[16]—was seen in

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all cases. However, the spectral profiles in the 1500–1800 cm^{-1} frequency range were practically unaffected by bromination, proving thereby that the structural modification introduced is mainly due to the formation of carbonyl groups. It should be stressed that during sulfonation special care was taken to remove O$_2$ from the sulfonation solution. However, the samples were kept in contact with air *after* sulfonation. Thus, the oxidation must have occurred during the purification stage and storage.

The breadth of the observed band and its multicomponent structure allows one to assume that the reaction between chlorosulfonic acid and the polymer results in the creation of several different carbonyl-containing species, both in the chain (like ketones) and end groups (like carboxylic acid). Wavenumbers of these functionalities fall into the frequency interval of 1640–1740 cm^{-1} [12] and are thus likely to be the origin for the spectral components at 1645, 1680, and 1715 cm^{-1}. A weaker band with higher frequency (1760 cm^{-1}) can be attributed to esters. In addition, complexes such as ROCOCl, with the characteristic frequencies at 1770–1800 cm^{-1}, may also be present. On the other hand, the broad band(s) with the lowest frequency (∼1590 cm^{-1}) may originate from the carbonyl groups involved in strong hydrogen bonding with sulfonic acid. Moreover, in this frequency region the band of asymmetric vibration of SO$_2$ groups in different organic sulfones, especially sulfonyl halides (ROSO$_2$X, X = F, Cl) and β-sultones, may appear. It is instructive to note that such species often appear because of the side reactions of the sulfonation.[17] Thus, on the basis of the consideration above we assign the high-frequency part of the observed profiles to the space-separated carbonyl groups but the low-frequency part to the contribution of the hydrogen-bonded (or confined) C=O groups and some SO$_2$-containing species other than sulfonic acid.

4. Effect of the Type of Irradiation and Radical Decay on the Side Reactions. In general, the band shapes in the 1500–1800 cm^{-1} region were similar in the studied samples in a such a way that neither visible frequency shift nor intensity redistribution between the components could be detected. The total integral intensity varied, however, significantly when comparing the nonirradiated samples to the irradiated ones. This means that the concentration and type of reactive radiolysis products have significant and detectable effect on the sulfonation products. To study the effect of the type of irradiation treatment on the amount of created carbonyl groups, the total integral intensities were normalized in the frequency region 1525–1825 cm^{-1}. The normalization was done with respect to the integral intensity of the characteristic band of the CH stretching vibrations (2750–3000 cm^{-1})—the band which was found to be unaffected by the sulfonation reaction. The obtained values are depicted in Figure 3. Thus, it shows the relative concentrations of the side products of the sulfonation reaction. It is seen that when PVF is sulfonated without irradiation treatment (marked as "n-i"), the concentration of side products of the sulfonation

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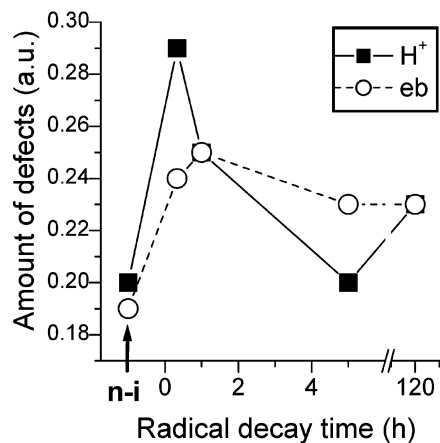

Figure 3. Amount of structural defects as a function of irradiation type and radical decay time. Absorbed dose of both samples was 400 kGy.

is comparatively low but is significantly higher in the irradiated samples. The samples subjected to the electron beam irradiation demonstrate stable behavior and the side-product concentration shows only a minor decrease within the 5 days of radical decay. In contrast, for proton-irradiated samples the overall rate of the side reactions significantly depends on the radical decay time. The highest concentration of the side products is achieved with the shortest radical decay time and the minimum value was obtained at 5 h of decay. After 5 h of decay the concentration is as low as that with the nonirradiated samples. Finally, after 5 days of decay the value for the side-product concentration is equal to the values of the electron beam-irradiated samples. Before going into the explanation of these unexpected results, we note that similar results were always obtained after repeating three times both the sample preparation and the analysis.

The relative amount of side products of the sulfonation reaction is the lowest in the nonirradiated samples. The amount is slightly higher in the samples that are essentially free from the radicals, that is, the samples with 5 days of decay. This means that the decay products of radicals are sensitive to oxidation. This can be explained by the oxidation of the formed double bonds upon radical decay. In the case of samples which contained also radicals the interpretation is more uncertain. As both types of irradiation produce similar kinds of radicals upon decay, the type of radicals can hardly be the main reason for the difference in the number of side reactions between the irradiations. Therefore, the most likely reason is the effect of the local concentration of radicals.

To study more closely the influence of radical decay time and the type of irradiation on the amount and kind of created C=O groups, we analyzed infrared difference spectra, which were obtained by the subtraction of the spectrum of nonirradiated sample from those of irradiated ones (i.e., $I_{(samp.1-4)} - I_{(samp.5)}$ and $I_{(samp.6-9)} - I_{(samp.10)}$). Thus, the obtained curves eliminate to a large extent the effect of such sulfonation reactions, which do not involve any radiolysis products. The IR difference spectra for the series of proton-irradiated membranes as a function of radical decay time are shown in Figure 4A. It is seen that both low- and high-frequency parts of the complex profile rapidly decrease in intensity
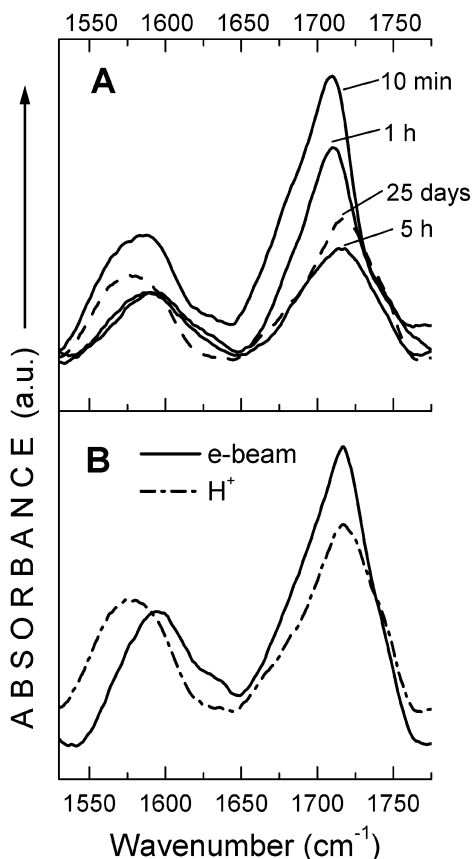
Figure 4. IR difference spectra of the sulfonated membranes (see text for explanation): (A) proton-irradiated membranes with different radical decay times; (B) effect of the type of irradiation.
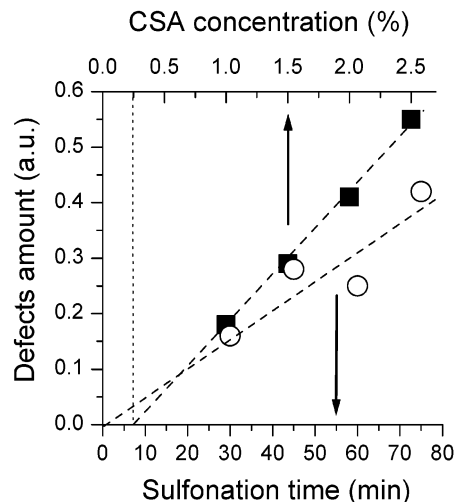

Figure 5. Amount of structural defects as a function of CSA concentration (sulfonation time is 60 min) and sulfonation time (at CSA concentration of 1.5%). All samples were proton-irradiated (dose 400 kGy; RDT, 1 h).
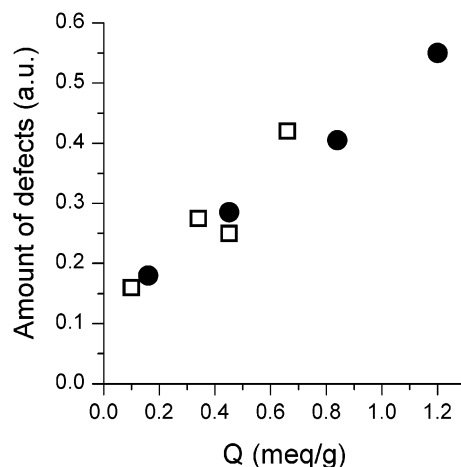

Figure 6. Dependency of the relative amount of side reactions on the sulfonation time (□) and chlorosulfonic acid concentration (●).

during 5 h of decay. This can be associated with the fast decay of aliphatic radicals and, as a consequence, decrease in matrix reactivity. Moreover, comparing the curves corresponding to 1 and 5 h of radical decay time, it can be concluded that the fraction of hydrogen-bonded carbonyl groups and $-SO_2$-structures decreases faster than that of space-separated species. This effect is most likely due to faster reaction of the closely located radicals created along proton tracks present in the matrix. In the spectrum of the sample which was sulfonated after 5 days of radical decay time we note again an increase in both peaks. However, the maximum of the low-frequency component shifts toward smaller wavenumbers. This can be explained by the fact that after such a long radical decay time only the decay products of radicals are left. Consequently, further sulfonation of these may produce highly separated carbonyl groups.

Figure 4B compares IR difference spectra of the PVF samples sulfonated immediately after irradiation (samples 1 and 6). It is seen that not only the amount but also the type of carbonyl groups is dependent on the type of irradiation. Both spectra demonstrate similar peaks centered at 1715 cm^{-1}, which is associated with the C=O groups in different molecular environments. However, the low-frequency part of the spectra is significantly different. In the electron-irradiated sample we note the presence of several peaks characteristic of strongly bonded carbonyl groups (1600−1650 cm^{-1}). In contrast, the spectrum of the proton-irradiated membrane demonstrates essential contribution from the

$-SO_2$-structures, which are characterized by the lower frequencies.

5. Effect of the Sulfonation Reagent Concentration and Sulfonation Time on the Side Reactions. We studied also the effect of the sulfonation reagent concentration on the formation of side products. Figure 5 shows the relative concentration of the side products as a function of sulfonation time and chlorosulfonic acid concentration. It is seen that both dependencies have linear character. Interestingly, the extrapolated line for the acid concentration dependency does not pass through the origin. This suggests that the reaction between the polymer and the chlorosulfonic acid starts only at certain acid concentrations (about 0.25%). Such threshold behavior has been experimentally observed numerous times by us. We also stress that all membranes were sulfonated under conditions where the chlorosulfonic acid content in the sulfonation solution was 10 times higher than necessary for the final reaction level. The explanation for the required minimum concentration of chlorosulfonic acid can be simply the fact that at low concentrations chlorosulfonic acid reacts rather with 1,2-dichloroethane or some possible impurities.
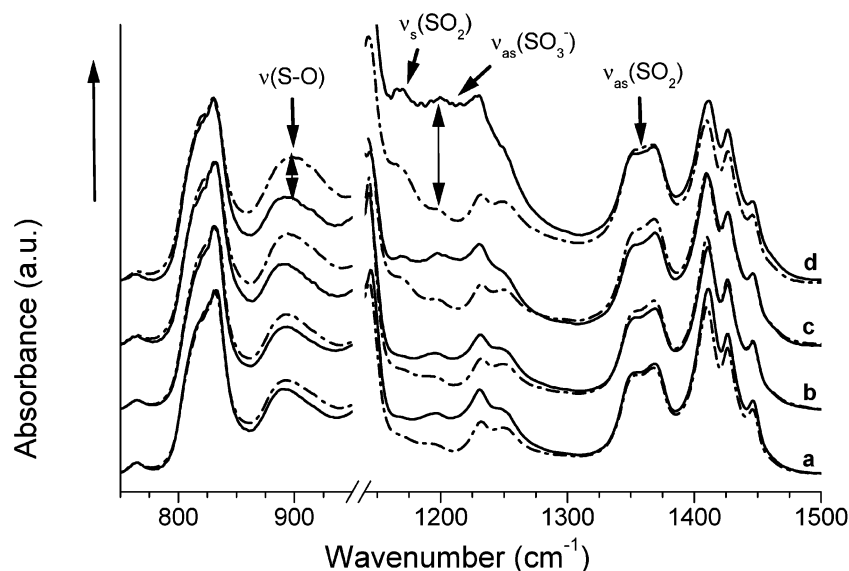
Figure 7. FTIR spectra of selected membranes in fully hydrated (solid) and dry (dashed) states in the characteristic frequency range of different SO vibrations: a, nonirradiated membrane (#10); b, electron-irradiated (#1); c, proton-irradiated (#6); d, sulfonated with high chlorosulfonic acid concentration (#17). All spectra are normalized with the intensity of polymer bands around 825 and 1425 cm^{-1} and shifted by pairs along the *Y*-axis for better comparison.

One of the main purposes of this work was to find the optimal conditions for sulfonating irradiated PVF films, that is, to avoid side reactions. In Figure 6 the relative concentrations of side products are given as a function of ion exchange capacity for proton-irradiated samples. The results are given both for different chlorosulfonic acid concentration and different sulfonation time. As shown, the concentration of side products can surprisingly be taken to be equally dependent on these variables when comparing the samples with the same ion exchange capacity. This means that with the studied irradiation treatments and decay times the sulfonation process can only be optimized by changing the radical decay and type of irradiation treatment.

6. Semiquantitative Analysis of the −SO$_3$H Concentration. Figure 7 compares FTIR spectra of several samples in hydrated and dry states (characteristic frequencies of sulfonic species are indicated on the top). When the polymer membranes are dried, the fixed ions are −SO$_2$OH groups with two S=O bonds and one S−OH. In the hydrated state, however, these groups dissociate and −SO$_3^-$ ions with three identical S−O bonds are present. Unfortunately, it was practically impossible to carry out quantitative analysis of the spectra because of the strong overlap between characteristic SO$_3$ peaks and polymer mode. However, it is possible to make some additional conclusions on the sulfonation reaction on the basis of these results. Molecular vibrations of these two forms are quite different. Thus, comparing the spectra of dry and hydrated membranes, one may evaluate the extent of hydration and the relative amount of sulfonic acid groups. It is seen from Figure 7 that all investigated samples demonstrate variation of spectral intensity, namely, change of absorption intensity in the regions around 1200 and 900 cm^{-1} with hydration and drying (marked with two-sided arrows). The extent of this alteration is, however, dependent on the procedure of the sample preparation. In the case of nonirradiated (plot a) and electron beam-irradiated sample (plot b)

after sulfonation, one may see only quite small growth of absorption. In contrast, a clear increase is observed with the proton-irradiated membrane (plot c). The materials sulfonated after proton irradiation in the solution with high chlorosulfonic acid concentration (plot d) show even stronger changes in the adsorption. The direct conclusion is the fact that with proton irradiation and high ion exchange capacity the hydration of the sulfonic acid groups is more extensive than in samples without irradiation treatment or membranes irradiated with an electron beam. This can be explained by the linear and sulfonic acid-enriched channels present in the proton-irradiated samples. However, such a conclusion is not supported by the ion exchange capacity results. The samples with the same sulfonation conditions and sulfonation time (sample numbers 1, 6, and 10 in the table) but different irradiation treatment had the same ion exchange capacity. Therefore, we conclude that the results presented in Figure 7 combined with the ion exchange capacity results are due to the fact that proton irradiation followed by sulfonation produces structures which are not detected in the initial ion capacity analysis. This is most likely due to the formation of derivates of sulfonic acid.

Conclusions

Local radical concentrations of the different types of radicals were concluded to be the most significant parameter in the sulfonation of PVF films. The effect of the optimal radical concentration was observed both in the extent of side reactions and in the formation of sulfonic acid derivates. Therefore, we suggest that polyenyl radicals are participating in such reactions which produce derivates of sulfonic acid like sulfonyl chlorides and β-sultones. Normally, these derivatives are easily converted to sulfonic acid after being in contact with water. In our case this can be limited because of the possibility of separation of these structures within the hydrophobic phase. More precisely, these separated areas can be located in the short and

separated spurs of radiolysis tracks enriched with polyenyl radicals. The formation of $-SO_2Cl$ and β-sultones with low accessibility of water is further explained by the fact that dichloroethane, which was used as the solvent in the sulfonation, is clearly the better solvent to the PVF than water. However, the final conclusion of the presence of sulfonic acid derivates was mainly based on indirect analysis and thus the prepared materials need to be studied further.

The scope of this work was to find the optimal conditions for the homogeneous sulfonation of PVF films.

According to the results, we can conclude that the most significant parameters are the type of irradiation and radical decay. In contrast, the combination of sulfonation time and chlorosulfonic acid concentration can be chosen rather freely. Note that this statement is valid only for bulk materials. Therefore, when preparing for example homogeneously sulfonated membranes, the concentration of sulfonation reagent has to be rather low to avoid over-sulfonation of the surface.