# Characterization of Radiation-Grafted Polymer Films Using CP/MAS NMR Spectroscopy and Confocal Raman Microscopy

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**ABSTRACT:** Preirradiated poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) base film were grafted with different amounts of an α-methylstyrene (AMS) and methacrylonitrile (MAN) copolymer. The molar ratio of AMS and MAN in the grafted polymer was determined using $^{13}$C-CP/MAS NMR spectroscopy and compared with the molar ratio determined with FTIR spectroscopy. The distribution of the components across the thickness of the grafted films was determined using confocal Raman microscopy. The validation of the confocal Raman microscopy was performed with FEP films grafted with MAN only, where pronounced grafting fronts were observed. The local degree of grafting for AMS/MAN co-grafted FEP films was calculated for each sample based on the intensity profiles, taking the mass of the grafted polymer and its molar ratio into account. The grafting of the AMS/MAN co-grafted films was found to be homogeneous over the thickness, even in case of small amounts of the copolymer (15 mass%). The homogeneity of the grafting across the film thickness is a prerequisite to obtain sufficient proton conductivity after sulfonation of the radiation-grafted films. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

**Key words:** fuel cells; radiation-induced grafting; copolymerization; NMR spectroscopy; confocal Raman microscopy

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*Dedicated to the memory of Prof. Klaus Müller*

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## INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are clean and efficient energy converters, operated at temperatures between 60 and 100°C, and, due to their low weight and fast start-up capability, considered as power sources for applications with variable load profile and intermittent operation, such as backup power sources or electric cars. The reliability of PEFCs strongly depends on the longevity of the polymer membrane and the catalyst, including its support. Currently, the requirements concerning performance are closest fulfilled by perfluorinated sulfonic acid membranes, for example, Nafion®, Flemion®, and Aciplex®. However, these state-of-the-art membranes are still too expensive for commercial use in fuel cells for most applications, and therefore, less costly membranes are under development.

A potentially cheaper way to produce proton conducting polymer membranes is the radiation grafting of commercially available, perfluorinated, or partially fluorinated base films with suitable monomers. The irradiation can be carried out simultaneously[1] or prior to grafting of the monomer onto the base film (preirradiation). Furthermore, the preirradiation grafting can be performed in air or inert gas.[2] Proton conductivity is introduced either by grafting of monomers carrying the sulfonic acid group or by post graft modification, for example, sulfonation, of the grafted compound.[3] The preirradiation grafting in air was chosen in the present work due to the lower requirements regarding the reaction process, compared to the handling of inert gas, and the absence of homopolymer formation for the present monomer combination. Homopolymer is not covalently bonded to the base film and is formed due to chain transfer reactions to the monomer (preirradiation method) or direct activation of monomers in the case of simultaneous irradiation.
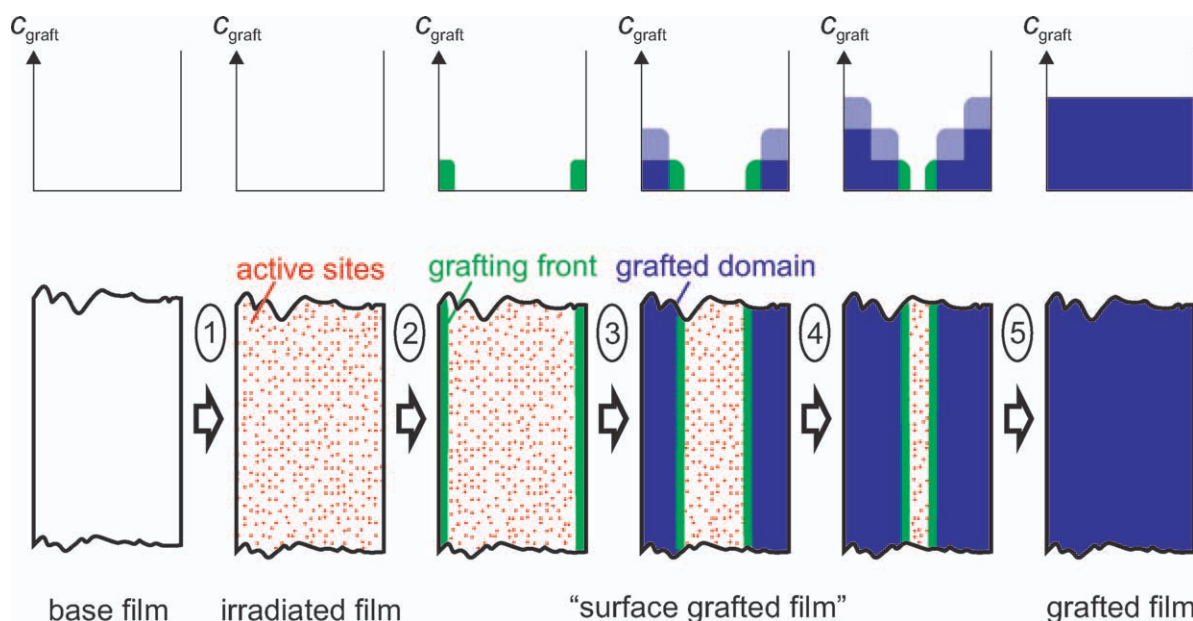
**Figure 1** Irradiation (1) yields active sites (radicals, dots) within the base film. Grafting is initiated at the surfaces by polymerization of monomers (2). Further grafting (3) from active sites within the irradiated film requires diffusion of monomers through the already grafted (swollen) polymer zone. Thereby, the grafting front moves from the surface to the interior and the formed grafted domain consists of previously grafted (dark shades) and later on added graft component (light shades). Termination begins in surface near areas and further grafting (4) increases the concentration of graft component $c_{\text{graft}}$ at the film center. Grafting for a sufficiently long time (5) yields homogeneously grafted films with the same $c_{\text{graft}}$ over the entire film thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Independent of the method, the grafting reaction occurs according to the front mechanism, if the pre-irradiated base film does not swell in the grafting solution (Fig. 1).[4]

To obtain reasonably good through-plane proton conductivity of membranes (for fuel cell applications $\sim 100$ mS cm$^{-1}$),[5] prepared by sulfonation of the radiation grafted film, the sulfonic acid groups have to be distributed over their entire thickness ("grafted film" in Fig. 1). The yield in grafting reactions is usually termed degree of grafting (DG) or graft level, which is defined as the mass based ratio of the added graft component and the initial base film according to

$$\text{DG} = \frac{m_{\text{graft}} - m_0}{m_0}, \qquad (1)$$

where $m_{\text{graft}}$ is the mass of the grafted film and $m_0$ corresponds to the mass of the irradiated base film. To account for the time dependency of the grafting, which is required, for example, to compare the kinetics of the graft polymerization under varied preparation parameters, such as temperature, concentration, monomers, nature of base films, the grafting process has been modeled and validated against the experimental data. The model included the parameters initial polymerization rate $r_{\text{p0}}$, termination of the chain growth by recombination with the rate $\gamma$, and movement of the grafting front from the

surfaces to the center of the preirradiated film with the constant velocity $v_d$.[6–8]

In the context of the development of radiation grafted membranes for fuel cells, we found that membranes based on co-grafted α-methylstyrene (AMS) and methacrylonitrile (MAN) can show enhanced stability under fuel cell conditions compared to styrene grafted membranes.[9,10] For such co-grafted systems, the DG alone is insufficient to characterize the proper composition of the grafted film. Therefore, the ratio of the monomer moieties in the grafted polymer has to be additionally determined. The insolubility of grafted poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)-based films restricts the number of suitable characterization methods. FTIR spectroscopy can yield the monomer ratio in the grafted film. Therefore, the signal intensities arising from the AMS and the MAN monomer units in the grafted chains, respectively, were determined and the ratio was calculated using a previously recorded calibration curve.[10] A difficulty associated with FTIR spectroscopy is the expansion of the film during grafting, which necessitates a correction of the measured intensities based on the area change. As a complementary method to characterize polymers, solid state NMR spectroscopy can be applied. Methods to investigate perfluorinated membranes, despite the difficulties given by their insolubility or the handling of thin films, were described in literature. A review on perfluorinated ionomers was, for

example, given recently by Heitner-Wirguin.[11] Therein, among others, $^1$H- and $^{19}$F-NMR spectroscopic investigations of, mostly solvent swollen, membranes were described. Solid state $^{13}$C-NMR spectra of fluoropolymers were recorded by Liu and Schmidt-Rohr.[12] They performed cross-polarization (CP) high speed magic angle spinning (MAS) experiments, with spinning frequencies $\omega_r$ higher than 25 kHz, to obtain narrow $^{19}$F signals by reducing the $^{19}$F-$^{19}$F and $^{19}$F-$^{13}$C dipolar couplings. The chemical degradation of perfluorosulfonic acid ionomer membranes was studied by Ghassemzadeh et al. using solid-state $^{19}$F- and $^{13}$C-NMR spectroscopy.[13]

The determination of the homogeneity of the grafted film necessitates an analytical method capable of resolving the local composition in both lateral, that is, over the film area, and thickness direction of the film. Confocal Raman microscopy[14–16] was shown by Mattsson et al. to allow investigation of the distribution of (a) styrene in PVDF grafted with styrene sulfonic acid (SSA) and (b) styrene and divinylbenzene (DVB) in PVDF-g-[SSA-co-DVB] over the membrane thickness.[17] The degradation of uncrosslinked membranes during fuel cell tests was shown to be homogeneous over the entire thickness.[18,19] The degradation of PVDF-g-SSA-, FEP-g-SSA-, and ETFE-g-SSA-based membranes was analyzed using confocal Raman microscopy by Kallio et al. and compared with results obtained with SAXS and WAXS.[20] They observed the almost complete loss of PSSA side chains and could correlate the extent of degradation with the water uptake of the membrane. Depth profiles of graft polymer membranes were recorded with a depth resolution of <0.6 µm using confocal laser scanning microscopy by Schmidt et al.[21] The measuring of depth profiles via confocal fluorescence microscopy was faster than micro-Raman profiling with the same signal-to-noise ratio, but staining of membranes with fluorescent dyes was necessary.

## EXPERIMENTAL

### Preparation of grafted films

Radiation-grafted membranes based on FEP (Teflon® 100A, DuPont, Circleville, OH) with 25 µm thickness were prepared using the procedure reported earlier.[9,10] The FEP films were electron beam irradiated to a dose of 25 kGy and stored at a temperature of −80°C. The preirradiated films were immersed into a grafting solution, consisting either of 30 vol % MAN (99%, stabilized with 50 ppm monomethyl ether hydroquinone, Aldrich), 20 vol % water (>18.2 MΩ cm, Labpure®), and 50 vol % isopropanol (>99.8%, Fluka) for the grafting of MAN only, or 30 vol % AMS (99%, stabilized with 15 ppm 4-(tert-

butyl)catechol, Aldrich) and MAN, at a molar ratio $R_{m,sol} = n_{AMS}/n_{MAN}$ of 1.5, 20 vol % water, and 50 vol % isopropanol for the co-grafting of AMS and MAN. Grafting was performed at a temperature of 50°C, and grafted films were prepared with different DG by varying the reaction time. The molar ratio of the monomer units in the grafted polymer $R_{m,graft}$ was determined by FTIR spectroscopy and calculated from the ratio of the molar amount of AMS and MAN. The spectra were recorded at 4 cm$^{-1}$ resolution in the mid-IR spectral range between 4000 and 400 cm$^{-1}$ with a Perkin Elmer FT-IR System 2000 spectrometer und evaluated with the curve fitting GRAMS/AI software, version 8.00 (Thermo Electron, Waltham, MA). AMS was quantified using the aromatic C=C-stretching vibration at 1498 cm$^{-1}$ and MAN using the C≡N-stretching vibration at 2235 cm$^{-1}$.

### Determination of the molar ratio of the monomers in the grafted film $R_{m,graft}$ by $^{13}$C CP/MAS NMR spectroscopy

Solid-state NMR experiments were performed on a Varian InfinityPlus 400 NMR spectrometer operating at $^1$H- and $^{13}$C-NMR frequencies of 399.76 and 100.53 MHz, respectively. The present experiments were done with a T3 HXY 4 mm MAS probe at a sample spinning speed of 13 kHz to suppress all spinning side bands in the $^{13}$C-NMR spectra. All $^{13}$C {$^1$H} NMR spectra were recorded using a ramped CP sequence with a contact time of 5 ms, if not stated otherwise.[22] The ramp was linear and was adjusted to cover the central Hartmann-Hahn match. The excitation pulse length for $^1$H was 4 µs. The signal acquisition of 10.24 ms was performed under CW decoupling with a $^1$H decoupling power of 75 kHz. The $^{13}$C {$^1$H} CP/MAS spectra were recorded using a recycle delay of 3 s, which was chosen on the basis of the results from $^1$H-T$^1$ measurements. Between 2000 and 8000 scans were used to accumulate the $^{13}$C signals, depending on the DG. For the single pulse $^{13}$C {$^1$H} NMR spectra 12000 scans were accumulated with a recycle delay of 15 s.

### Determination of the local degree of grafting (DG$_{local}$) by confocal Raman microscopy

The measurements were performed on an alpha300 R confocal Raman microscope linked to a UHTS 300 spectroscopic system (WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm/Germany) in combination with an oil immersion objective (Zeiss 100×, NA = 1.4) and immersion oil (Merck, $n$ = 1.52). A Nd:YAG Laser ($\lambda$ = 532 nm, $P$ = 4 mW) was used for the excitation. A grating with 600 grooves per millimeter enabled the measurement of the spectral range between roughly −300 and

3500 rel. cm$^{-1}$ with the spectral center at 1900 rel. cm$^{-1}$. The lateral resolution is given by the diffraction limit $d$:

$$d = \frac{\lambda}{2(n \sin \theta)},$$

where $\lambda$ is the wavelength of the laser, $n$ the refractive index of the immersion oil, and $\theta$ the aperture. The term $n \cdot \sin \theta$ is the numerical aperture and corresponds to the numerical value 1.4 of the used oil immersion objective. Taking the wavelength of the laser into account (532 nm), the diffraction limit $d$ is 190 nm. According to Juang et al., a depth resolution of around 0.3 μm can be reached using the experimental setup with an oil immersion objective and immersion oil with a refractive index of 1.515.[23] The refraction indices of the measured films were estimated to be in the range from 1.4 to 1.5, as the true values were experimentally not accessible. Furthermore, according to Everall, the depth resolution in confocal microscopy depends on the penetration depth.[15,16] Because of the unknown exact refractive index of the films, the experimental setup was validated with an anisotropically grafted film. The anisotropy was caused by the adhesion of the film to the glass wall of the reactor during the grafting process. Hence, the film was grafted only on one side in the surface-near region. The grafting profile was investigated from both sides of the anisotropically grafted film and the grafted region was found to be identical in thickness and in the intensity of the MAN based C≡N vibration, independent of the direction of the measurement. In addition, the absolute thickness of each grafted film was measured with a thickness gauge and was in all cases confirmed by the confocal Raman microscopy with an accuracy of ±1 μm. Hence, the optical resolution given by the manufacturer of the microscope was confirmed and assumed to be diffraction limited, 200 nm laterally and 500 nm vertically, and a spectral resolution down to 0.02 cm$^{-1}$ was possible. The Raman microscope was equipped with a linear, piezo-driven, feedback-controlled scan stage. The accuracy is specified by the supplier with 4 nm laterally and 0.5 nm vertically and the position is controlled on all axes using capacitive sensors. The spectra and profiles were evaluated and post processed with WITec Project software (Vers. 1.92). Because of the scattering losses, a correction of the intensity profiles was necessary. Therefore, the intensity of the C—F vibration was used as internal standard, assuming to either be constant over the entire film thickness for homogeneously grafted films or at least identical at mirrored positions in both directions from the film center assuming the presence of grafting fronts. A linear approximation was used to fit the decrease of the C—F vibration intensity over the film thickness. The slope of the approximated line was used to correct the intensities of FEP, AMS, and MAN. To minimize the influence of lateral inhomogeneities, the 31 spectra measured at each depth were averaged and the intensity of the signal was determined for each compound and added up over the entire thickness. The summation yielded the integral intensity, which was associated with the integral mass of the corresponding component. This integral mass was calculated based on the DG in case the films were grafted with MAN only, and based on the DG and $R_{m,\text{graft}}$ for films co-grafted with AMS and MAN. The local mass for each compound at a given depth was calculated from the ratio of the integral intensity and the intensity at the corresponding depth. Finally, the local degree of grafting DG$_{\text{local}}$ was calculated from the ratio of the local mass of MAN and FEP for the DG$_{\text{local}}$ of MAN, and in the case of co-grafted films additionally of the local mass of AMS and FEP for the DG$_{\text{local}}$ of AMS.

## RESULTS AND DISCUSSION

The grafting of the preirradiated FEP base films with either MAN only or AMS and MAN is discussed in detail elsewhere.[9,10] The time dependence of the DG is shown in Figure 2 by reaction profiles of the graft polymerization of MAN only and the copolymerization of AMS and MAN onto FEP base films. The experimental data (circles in Fig. 2) were fitted (lines in Fig. 2) using a simple kinetic model as described above.[6,7]

NMR signal intensities are frequently used to determine the relative amounts of the resolvable structural units in the samples under investigation. For solid state NMR experiments under CP conditions, this simple approach might be accompanied by substantial errors, because the underlying $^{1}$H-X polarization transfer (X = heteronuclei with low natural abundance, such as $^{13}$C, $^{29}$Si, etc.) strongly depends on the local chemical environment (e.g., proton density, internuclear distances) of the examined heteronucleus. Several experimental approaches exist to overcome this basic problem, as, for instance, the use of the quantitative cross polarization (QUCP) sequence,[22] but up to now no generally applicable technique has been proposed. For individual systems, it might be possible to achieve quantitative conditions by applying an amplitude ramp on one of the channels during the contact time (RAMP-CP)[24] as also done in the present work.

$^{13}$C-CP/MAS NMR spectra recorded for FEP films grafted with MAN (not shown) and co-grafted with AMS and MAN were used to assign all signals to the different carbon sites in the grafted side chains. The peaks labeled with 1–4 were present in the
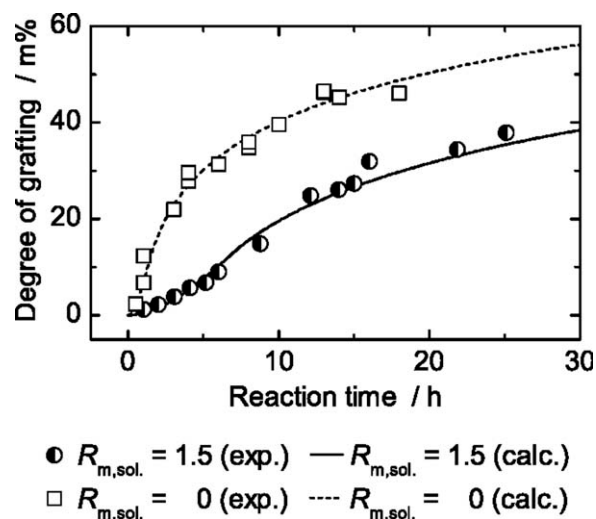
**Figure 2** Time dependent degree of grafting (reaction profiles) for FEP-*g*-MAN (□) and FEP-*g*-[AMS-*co*-MAN] (◑). The symbols refer to measured values and the lines correspond to fitted curves, calculated based on a simple model.[6,7]

spectrum of FEP-*g*-MAN and were assigned to the carbons in the MAN repeating unit on the basis of their chemical shifts (Fig. 3). The additional signals A-E observed in the spectrum of FEP-*g*-[AMS-*co*-MAN] were attributed to the carbon atoms in the AMS repeating unit. The ortho, meta, and para positions of the phenyl ring (label "E") present in the AMS repeating unit could not be resolved and overlapped with the signal of the cyano group (label "3").

In principle, all peaks in Figure 3 could be used to quantify the AMS/MAN-ratio. However, the best peak separation was observed for the two quaternary carbons in alpha-position to the phenyl ring (assignment B in Fig. 3, 42 ppm) and next to the cyano group (assignment 2 in Fig. 3, 33 ppm).
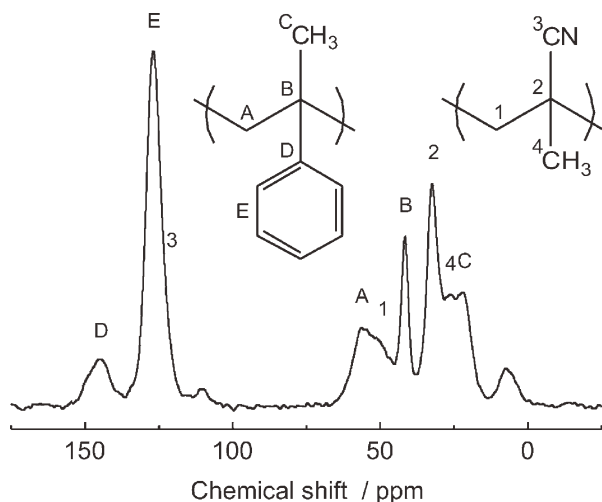
To validate the possibility of a quantitative determination of the AMS:MAN molar ratio by analyzing the respective resonances under CP/MAS conditions, a series of CP/MAS spectra was recorded as a function of the contact time. The peak areas for the signals at 33 and 42 ppm were determined by spectral deconvolution of the region between 0 and 70 ppm using the NUTS NMR utility transformation software (Acorn NMR 2009, Livermore, CA). The respective cross polarization curves for these two resonances are plotted in Figure 4. It is found that the two curves are parallel over the whole range, as reflected by the derived constant signal intensity ratio. These results imply that for the present materials, the CP/MAS spectra can be analyzed in a quantitative manner, and it is possible to calculate the relative amounts of the two comonomers AMS and MAN.

Accordingly, the AMS : MAN molar ratio was determined for five AMS/MAN co-grafted FEP films with different DG, based on the analysis of the respective CP/MAS NMR spectra (using a contact time of 5 ms). The results are summarized in Table I and compared with the values obtained from FTIR spectroscopy. In addition, single pulse ^{13}C MAS NMR spectra (see spectrum in Fig. 5) were recorded for two representative samples. The derived values are in good agreement with those derived from the CP/MAS NMR spectra.

The standard deviation of the molar ratio $R_{m,\text{graft}}$ was found to be ±5 % for the FTIR spectroscopy based and ±6 % for NMR spectroscopy based values shown in Table II. The difference of the $R_{m,\text{graft}}$ values for the same sample, determined by the two different spectroscopic methods, is less than 5%.



**Figure 3** ^{13}C CP/MAS NMR spectrum of an FEP-*g*-[AMS-*co*-MAN] film with 35 % degree of grafting.
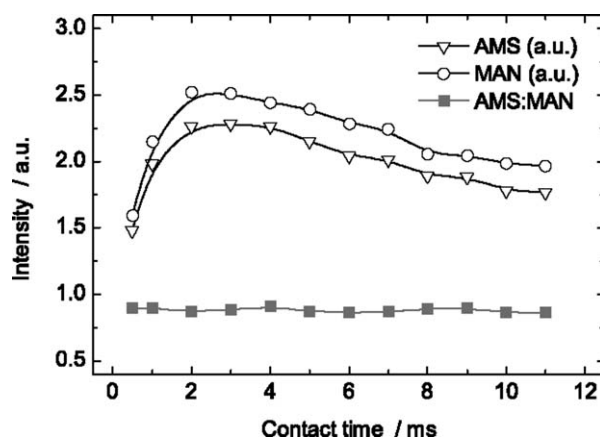


**Figure 4** [13]C CP curves for an FEP-*g*-[AMS-*co*-MAN] film with 34% degree of grafting. The intensities (peak area) of the AMS based quaternary carbon (peak "B" in Fig. 3) and MAN based quaternary carbon (peak "2" in Fig. 3) are shown in common arbitrary units. The filled symbols represent the AMS:MAN molar ratio derived from these CP curves.

## TABLE I
### Comparison of the AMS:MAN Molar Ratios Determined with FTIR Spectroscopy and NMR Spectroscopy, Either in CP or Single Pulse Experiments
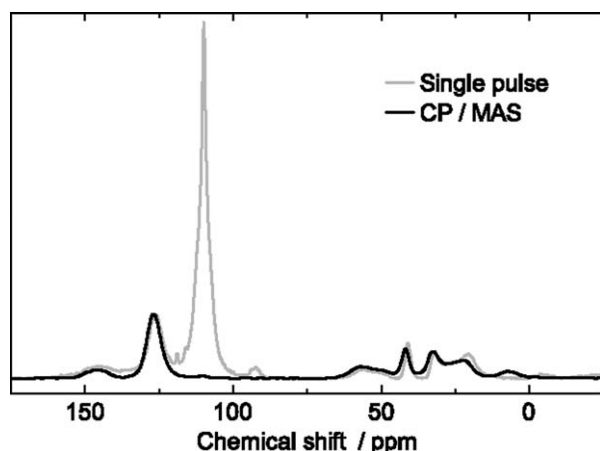
| | Molar ratio in the grafted polymer $R_{m,\text{graft}}$ | | |
|---|---|---|---|
| DoG (m %) | FTIR | CP | Single pulse |
| 5 | 0.84 | 0.82 | – |
| 15 | 0.85 | 0.89 | – |
| 24 | 0.91 | 0.92 | – |
| 35 | 0.92 | 0.88 | 0.90 |
| 44 | 0.91 | 0.87 | 0.89 |

Based on the good agreement, the FTIR spectroscopic measurement is further used as routine method to determine the $R_{m,\text{graft}}$, owing to its simpler experimental setup. Nevertheless, NMR spectroscopy offers an alternative way to measure the $R_{m,\text{graft}}$. In the following, the NMR-based $R_{m,\text{graft}}$ is used to calculate the concentration profiles.

## DEPTH RESOLVED CONCENTRATION PROFILES

The Raman spectrum of an AMS/MAN co-grafted FEP film (DG = 32%) was measured by focusing $\sim$ 5 μm below the surface and accumulating data over 60 s integration time (Fig. 6). The correlation of the signals with the associated vibrations and their assignment to a repeating unit of the grafted film was carried out by comparison of spectra of FEP base film, FEP-g-MAN, and FEP-g-[AMS-co-MAN] films (spectra not shown in detail).

The integration of the peak area was found to yield more reproducible results than the determination of the peak maximum. For this reason, all following quantitative data are based on the peak
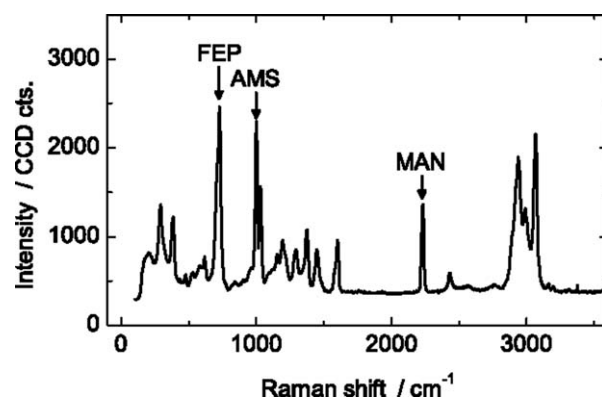
## TABLE II
### Raman Active Vibration Bands and Integration Boundaries Used to Determine the Intensities of the Different Components in Grafted Films

| | | Integration boundaries ($\text{cm}^{-1}$) | |
|---|---|---|---|
| Component | Peak maximum ($\text{cm}^{-1}$) | Lower | Upper |
| FEP | 730 | 660 | 780 |
| AMS | 1030 | 1015 | 1065 |
| MAN | 2235 | 2180 | 2300 |

area and, therefore, the integration boundaries are denoted in the last two columns of Table II.

Depth resolved intensity profiles of either MAN grafted alone or AMS/MAN co-grafted onto FEP films were recorded with 5 s integration time per spectrum. To prevent wrinkling of free standing films, double faced adhesive tape was used to attach the films to a glass plate. The maximum lateral displacement (180 μm) of the microscope stage was utilized to record 31 spectra, one spectrum every 6 μm. The measured depth was adapted to the thickness of each sample and measurements were performed in 1 μm steps. The measurement was started about 5 μm above the upper and stopped about 5 μm below the lower surface, due to problems with focusing on the surfaces. The film thickness was finally defined via the intensity of the C—F-vibration related to the FEP backbone.

Depth profiles of FEP films grafted with MAN only in the DG range from 0% (FEP base film) to 46% are shown in Figure 7. The thickness of the grafted films was determined by the C—F vibration of the FEP moiety. Especially, the weakly grafted films (<15%) call for the need for the thickness definition via the C—F vibration intensity. Although the intensity of the C≡N vibration is too weak to define



**Figure 5** Single pulse $^{13}$C (gray) and $^{13}$C CP/MAS NMR spectrum (black) of FEP-g-[AMS-co-MAN] with 35% degree of grafting.



**Figure 6** The signals used to quantify FEP (728 $\text{cm}^{-1}$), AMS (1030 $\text{cm}^{-1}$), and MAN (2235 $\text{cm}^{-1}$) are labeled in the Raman spectrum of an FEP-g-[AMS-co-MAN] film with 32% degree of grafting.
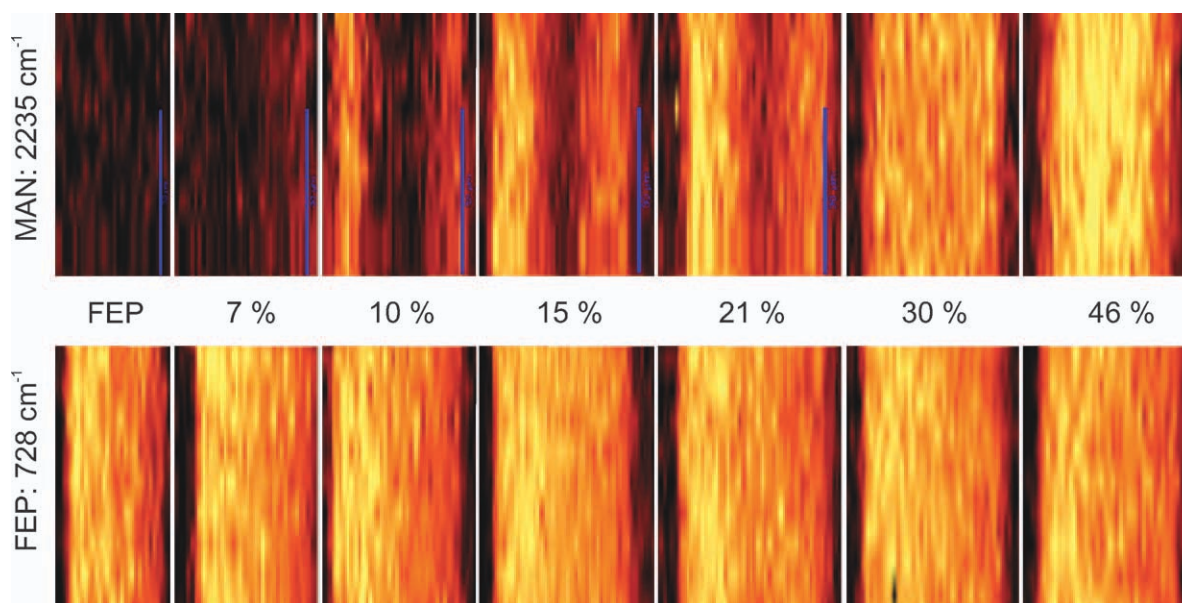
**Figure 7** Intensity profiles of MAN grafted FEP films with different degrees of grafting. The intensity of the CN stretching vibration (2235 cm$^{-1}$) of the grafted polyMAN is shown in the upper row and the CF stretching vibration of the FEP base film (728 cm$^{-1}$) in the lower row. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surfaces, the more intense C—F vibration allows the determination of the film thickness. The thickness increases significantly with the DG from 25 μm for the FEP base film to about 40 μm for the film with 46% DG.

The intensity of the MAN based C≡N vibration is very weak for the sample with 7% DG, increases up to 15% DG in the surface near area, and shows noticeable intensity in the film center for samples >21% DG. The intensity of the C≡N vibration and, therefore, the concentration of MAN moieties seem homogeneously distributed over the entire film thickness for the sample with 30% DG and slightly higher in the center of the film grafted at 46% DG. The presence of a surface-near domain, which includes a comparatively high intensity of the C≡N vibration for low DG, and its growing toward the center of the film with increasing DG indicates the grafting of MAN according to the front mechanism (Fig. 1).

In contrast to the films grafted with MAN only, all AMS/MAN co-grafted films show, independently of the DG, homogeneously distributed graft components (Fig. 8).

The DG$_{local}$ was calculated according to the above described procedure and is plotted as a function of the relative depth in concentration profiles (Figs. 9 and 10). The relative depth corresponds to the measured depth, only the zero position was shifted. The shift was chosen for comparison reasons and, therefore, the film center located at the same position, which was chosen at 25 μm for MAN only (Fig. 9)

and at 20 μm for AMS/MAN co-grafted films (Fig. 10). Different concentration profiles were obtained for the grafting of MAN only and the co-grafting of AMS and MAN.

The onset of the MAN grafting at the surface, the simultaneous increase of the surface-near DG$_{local}$ and the propagation of the grafting fronts to the center is in agreement with the concept of the front mechanism (Fig. 9). The start of the grafting in the film center is obvious at 15% DG and a homogeneous distribution is reached at 30% DG.

As opposed to this result, concentration profiles obtained for AMS/MAN co-grafted films did not show grafting fronts (Fig. 10). In the measured DG range from 15 to 44%, the distribution of AMS and MAN was homogeneous over the entire film thickness. Furthermore, a film with 5% DG was investigated and no grafting fronts were detected. However, the signal-to-noise ratio at 5% DG was very low and close to the detection limit, for AMS as well as for MAN.

The results become more understandable by considering the different reaction times for grafting MAN only or co-grafting AMS and MAN (Fig. 2). After around 1 h, 15% DG$_{MAN,total}$ were grafted in case of grafting of pure MAN. Around this graft level the grafting at the film center set in and another 1.5 h later a homogeneous distribution was reached at around 30% DG$_{MAN,total}$. The co-grafting of 15% DG of AMS and MAN, which is the sum of DG$_{AMS,total}$ and DG$_{MAN,total}$, took around 6 h and 15 h in total were needed to reach 30% DG. Assuming
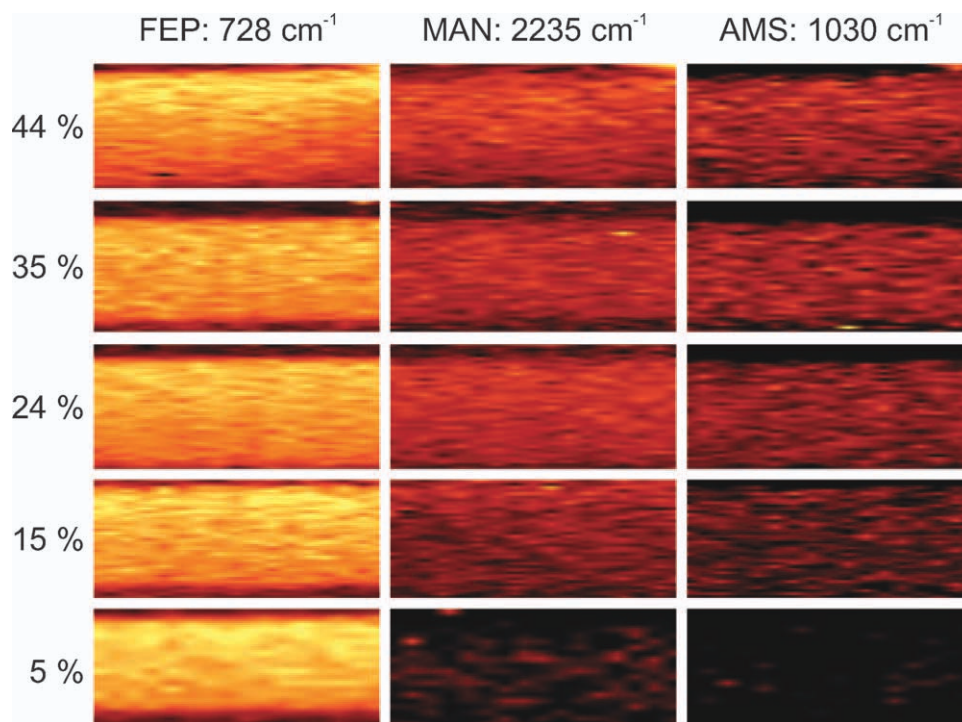
**Figure 8** The intensity of the CN stretching vibration (2235 cm$^{-1}$) of the MAN moiety, the CH stretching vibration of the AMS moiety (1030 cm$^{-1}$), and the CF stretching vibration caused by the FEP base film (728 cm$^{-1}$) of FEP-g-[AMS-co-MAN] are shown for five different degrees of grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

comparable diffusion coefficients for AMS and MAN in the grafted film, the observed difference in the depth profiles is a consequence of the slower copolymerization kinetics of AMS and MAN compared with the polymerization of MAN only. Therefore, the grafting of MAN appears to be diffusion limited in the initial phase of grafting, resulting in the appearance of a distinct grafting front, until a homogeneous distribution of grafts is reached at an overall graft level of around 30%. The slower co-grafting reaction of AMS and MAN seems to allow enough time for the diffusion of the monomers into
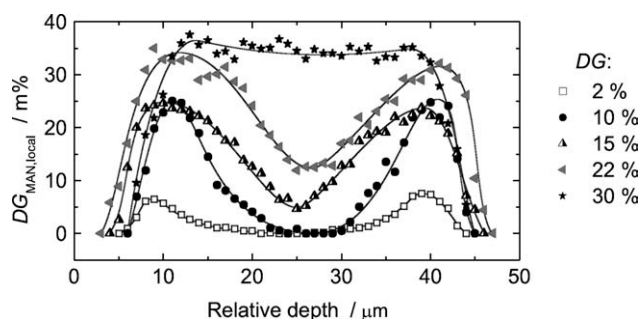


**Figure 9** Concentration profiles (DG$_{MAN}$ vs. relative depth) of MAN-grafted FEP films with different average graft level. The DG$_{MAN}$ was calculated based on the integral, mass-based degree of grafting and the intensity profiles (cf. Fig. 7).
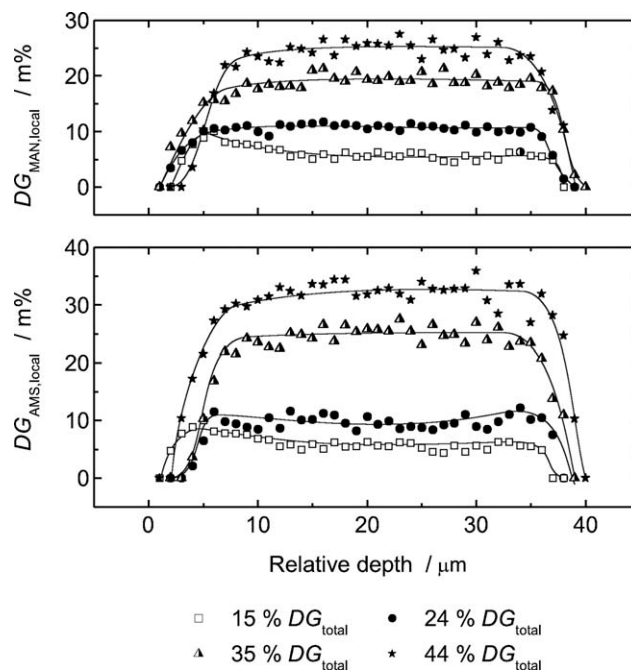


**Figure 10** Concentration profiles (DG$_{AMS}$ and DG$_{MAN}$ vs. relative depth) of AMS/MAN co-grafted FEP films with different degree of grafting. The DG$_{AMS}$ and DG$_{MAN}$ were calculated based on the integral, mass-based degree of grafting, the molar ratio determined by CP/MAS $^{13}$C-NMR spectroscopy (cf. Table I), and the corresponding intensity profiles (cf. Fig. 8).

the FEP film, thus resulting in the uniform increase of the degree of grafting over the film thickness.

## CONCLUSION

The determination of the influence of varied reaction parameters on the composition of grafted films and membranes requires analytical methods capable of resolving the expected changes. Because of the insolubility of grafted films, the characterization has to be done in solid state. The DG is an integral measure of the mass ratio between the added graft component and base film. The co-grafting of two or more monomers necessitates the determination of the ratio of the monomeric units in the grafted film or membrane. Solid state NMR spectroscopy was used to probe the molar ratio ($R_{m,\text{graft}}$) in AMS/MAN co-grafted films. The molar ratio in grafted films was determined by CP MAS $^{13}$C-NMR spectroscopy, using the ratio of the quaternary carbons in alpha-position to the phenyl ring and cyano group for AMS and MAN, respectively. The $R_{m,\text{graft}}$ values obtained by NMR were consistent with the FTIR spectroscopy data within $\pm 10\%$ relative standard deviation.

Raman microscopy in confocal setup is a suitable method to achieve a depth resolution of $\sim 1~\mu m$. The depth profiles recorded for the grafted MAN only and for co-grafted AMS and MAN are of considerable difference. The grafting of MAN shows the development of a pronounced grafting front up to a DG of 22%. The copolymerization of AMS and MAN, by contrast, does not result in the formation of grafting fronts, the fractional degrees of grafting for AMS and MAN appear to be largely uniform at all times. The difference in the distribution of the graft component is probably a result of the different grafting kinetics: the co-grafting of AMS and MAN is much slower compared to the grafting of pure MAN, which may render the co-grafting reaction limited, whereas MAN grafting appears to be diffusion limited, at least in the initial phase.

Nevertheless, the most important information from the confocal Raman microscopic investigation for the membrane preparation based on AMS/MAN co-grafted FEP films is the homogeneous distribution of AMS and MAN over the entire film thickness. This homogeneity ensures after sulfonation of the grafted films and subsequent hydrolysis sufficiently high through-plane proton conduction, even for films with low DG.

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