Depth Profiling of Graft Polymer Membranes via Confocal Laser Scanning Microscopy

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Confocal laser scanning microscopy is presented as a novel, quick, and facile technique for obtaining copolymer composition profiles of grafted polymer membranes. The nondestructive method requires only staining the membranes with a fluorescent dye and gives profiles of prepared membranes with high spatial resolution and good signal-to-noise ratio within a few minutes. For demonstration, depth profiles and distribution of graft polymer along the cross section of ETFE-*graft*-poly(styrene), ETFE-*graft*-poly-(4-vinylpyridine), ETFE-*graft*-poly(1-vinylimidazole) and FEP-*graft*-poly(styrene) films, prepared by the electron beam pre-irradiation technique, were determined. Measurements were conducted in reflection mode in the visible region and in fluorescence mode on dry membranes and on membranes stained with rubrene as fluorescent dye. The relative contents of graft polymer as obtained by this method are in good agreement with results from micro-Raman measurements. The presented new method poses an alternative to existing techniques for determining graft penetration profiles.

Introduction

Radiation induced radical graft polymerization is a well described method[1−6] offering interesting pathways for the synthesis of polymeric membrane materials that can be employed in a wide number of applications such as separation (e.g., pervaporation or desalination),[7−9] electrochemical devices (batteries, fuel cells, supercapacitors),[10−16] biomedicine (e.g., haemodialysis)[17−19] or environmental chemistry (like acid or salt recovery).[20,21] In most cases, the spatial distribution of the graft polymer within the membrane is of great importance for the suitability of the material for the particular application: For some separation purposes it is desirable that the graft polymer rather forms layers on the surfaces, whereas it should penetrate the matrix in the case of electrolytic membranes for proton exchange membrane fuel cells (PEMFCs). The determination of the spatial distribution, for example, as a concentration profile across a section through the membrane, is therefore of great interest especially with respect to the production processes of these membranes and to the optimization of process parameters.

To determine transversal concentration profiles, several techniques have been used in prior works, like micro-Raman spectroscopy (Renishaw spectroscopy),[22−24] step-scan Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS),[25−27] or in the case of distributed sulfonic acid groups, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS, "sulfur microprob-

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ing").[28,29] However, most of these methods require complicated sample preparation (e.g., cutting an imbedded membrane), lengthy measurement procedures, or intricate methods of interpretation (like finding appropriate IR or Raman bands and calculating the relations) and usually do not provide highly resolved profiles.

In this work, we present a new, alternative and nondestructive way to accurately determine high-resolution transversal concentration profiles in graft polymer membranes by applying fluorescence microscopy. The idea is to use intrinsic fluorescence of one of the copolymer components or the fluorescence of a deliberately added fluorescent dye to map the local concentration of the polymer components. By spatially resolved measurement of the fluorescence intensity and subsequent data analysis, it is possible to obtain concentration profiles with a spatial resolution comparable to that of the microscope. This can be done even without prior preparation of cut samples or slices, by employing a confocal laser scanning microscope (CLSM) equipped with an axial scanning stage (*z*-stage). The CLSM imaging routine presented in this paper thus poses a simple and fast method for obtaining highly resolved concentration profiles by circumventing the difficulties of sample preparation or acquisition and analysis of a huge number of spectra.

To use fluorescence for mapping the spatial concentration distribution of one polymer (the graft polymer) in another (the matrix), two main conditions have to be met:

1. One of the polymers shows intrinsic fluorescence in the experimentally accessible wavelength region or can selectively be labeled or stained with a fluorescent dye.

2. The fluorescence intensity has to be proportional to the (local) content of the respective polymer component.

In most copolymers, neither component exhibits intrinsic fluorescence in a wavelength region suitable for standard microscope optics. However, because of the great choice of fluorescent dyes, in almost any technically relevant case a dye can be found that is preferentially soluble in one of the components. Thus it is easy to satisfy the first condition.

The second condition is inherently met by most graft copolymers: When the grafted chains have a sufficiently high degree of polymerization, micro-phase separation occurs. Each phase, the one rich in matrix polymer and the one rich in grafted polymer, has a constant composition which is controlled solely by thermodynamics. When the overall composition varies, only the volume fractions of the two micro-phases vary accordingly. A fluorescent dye is distributed in the two phases with different concentrations according to its distribution coefficient. Because the size of the microphases is usually far smaller than the resolution of an optical microscope, the fluorescence intensity observed is an average quantity (on a micrometer scale) and a linear function of the volume fraction, which in turn represents the overall composition. Therefore, it is not necessary to determine absolute concentrations of the fluorophore if the total content of graft polymer is known from separate, for example, gravimetric, measurements.

It has been reported that graft polymerization in partially crystalline matrix polymers usually starts in the amorphous phase and does not change crystallinity up to composition ratios of 1:1.[30] As long as the crystalline phase is unchanged by the grafting process the expected proportionality is not affected. Only for high degrees of grafting, when the crystalline phase is changed, or in the case of low degrees of polymerization where micro-phase separation does not occur, significant deviations from proportionality or linear behavior must be expected.

One of this work's objectives is to show this proportionality between fluorescence intensity and content of the grafted polymer in the membrane material. The suitability of confocal fluorescence microscopy to determine transversal profiles of graft polymer content with a spatial resolution in the micrometer range is shown for four exemplary membrane systems obtained by radiation induced graft polymerizations: ETFE (poly(tetrafluoroethylene-*alt*-ethylene)) as the matrix polymer grafted with poly(1-vinylimidazole) (P1VIm) and poly(4-vinylpyridine) (P4VP) as intrinsically fluorescent components, and FEP (poly(hexafluoropropylene-*co*-tetrafluoroethylene)) and ETFE membranes grafted with poly(styrene) as nonfluorescent components that is selectively stained with rubrene (5,6,11,12-tetraphenylnaphthacene).

Series with increasing graft polymer concentrations were synthesized for each system, and the proportionality between fluorescence intensity and graft polymer content was verified by a comparison with gravimetric data. The profile curves were also compared to results obtained from established micro-Raman spectroscopy. The selective solubility of rubrene in poly(styrene) in the case of the dye-stained graft polymer samples can be shown directly from imaging data. Additionally, to make sure that the dye content reached its saturation value according to the solubility equilibrium, that is, that the diffusion of the dye into the membrane does not influence the measured fluorescence intensities, samples with different periods of staining were compared.

Experimental Section

Membrane Preparation. The commercial polymer films ETFE and FEP (Nowofol GmbH, Siegsdorf/Germany, thickness 50 μm and 40 μm, respectively) were irradiated under air by an electron accelerator employing energy doses of 50 kGy and 100 kGy.

For the grafting of styrene (distilled and stored at 4 °C) onto ETFE and FEP, a dose of 50 kGy was employed for activation. Styrene was deoxygenated by constant flow of nitrogen for at least 20 min and used without additional solvent. For the grafting of 4-vinylpyridine onto ETFE (activated by 100 kGy radiation), a 1:1 mixture (by volume) of monomer and dry tetrahydrofurane was deoxygenated by stripping with nitrogen and used for the polymerization. For grafting 1-vinylimidazole, the distilled monomer was used in bulk. The reactions were typically carried out in 10 mL glass ampoules with 4 mL of the reaction mixture and using pieces of the irradiated membranes of about 50 mg. After addition of the activated polymer films, the mixtures were again deoxygenated with a nitrogen flow for 5 min. The ampoules were sealed and put into a steel block preheated to 60 °C, thus starting the reaction. After polymerizing under constant shaking for the desired grafting period,

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the grafted film was removed from the mixture and residual monomer and homopolymer were extracted with a large excess of tetrahydrofurane (for removing styrene and its homopolymer) or methanol (for 4-vinylpyridine and 1-vinylimidazole and their homopolymers) for at least 24 h.

The obtained mass content w_g of graft polymer (in wt %) was determined gravimetrically according to eq 1.

$$w_g = \frac{m_g}{m_r} = \frac{m_r - m_0}{m_r} = \frac{\text{d.o.g.}}{1 + \text{d.o.g.}} \quad (1)$$

with m_0 representing the mass of the film before grafting (pure matrix polymer), m_g being the increase in mass due to the grafted polymer, m_r being the mass of the whole graft copolymer membrane (matrix + grafted polymer), and d.o.g. being the degree of grafting, that is, the increase in weight relative to the initial mass of the pure matrix polymer m_0 after drying the grafted films in vacuo to constant weight.

Treatment of FEP and ETFE Films for Microscopy. Samples of the films were cut into 2 mm × 5 mm strips for easy handling. As a result of intrinsic fluorescence of P4VP and P1VIm a preceding treatment of these samples with a fluorescence dye was not necessary.

The strips of the poly(styrene) grafted membranes were placed into an Eppendorf vessel containing a toluene solution of rubrene (20 μg rubrene/mL toluene). To ensure the complete diffusion of the dye, the mixture was stored for 48 h at ambient temperature. The strips were removed and dried cautiously on a paper towel, and each was placed onto a microscopy slide with a drop of water to improve contact and optical contrast. A cover slip was used to prevent solvent evaporation and to flatten the samples.

Micro-Raman Spectroscopy. A Raman spectrometer from Jobin Yvon LabRAM 1B (ISA DILOR SPEX) with an external Coherent Nd:YAG laser (532 nm, 100 mW) was used. The spectrometer was integrated in a confocal Olympus BX 40 microscope setup with an Olympus LWD objective ×50/0.50 (long focus) and a grating of 600 mm^{-1}. For interpretation of the acquired Raman spectra, the intensities of the characteristic poly(styrene) band at 3054 cm^{-1} and of the ETFE band at 2970 cm^{-1} were used after baseline subtraction.

Dye Saturation Test. A highly grafted ETFE-*graft*-poly(styrene) sample with 42.2 wt % of PS was cut into six 2 mm × 5 mm strips that were placed in an Eppendorf vessel with 500 μL of toluene. All samples were allowed to swell for 30 min before 10 μL of a rubrene solution (1 mg rubrene/mL toluene) were added. The samples were taken out 5 min, 10 min, 20 min, 80 min, and 24 h after addition of rubrene and were immediately examined following a procedure described below. A non-grafted sample was examined using same methods.

Confocal Fluorescence Microscopy and Data Analysis. A Leica CLSM with inverse optical setup DM IRBE, with TCS SP2 scanner and a scanning stage to allow for fast *x*, *z* scans, was used to obtain optical cross-sections of the films. The objective used was a 63× 1.2 NA water immersion objective. As a light source, the 488 nm line (for reflection images) and the 514 nm line (fluorophore excitation for fluorescence images) of an argon laser were used.

Each cross section (*x*, *z* plane) was imaged with a digital resolution of 512 pixels × 512 pixels. The size of the frames was 125 μm × 125 μm, corresponding to a pixel size of approximately 0.25 μm × 0.25 μm. The lateral optical resolution was about 0.2 μm for the wavelengths used for fluorescence mode and even better for the reflection mode. The transversal optical resolution was determined to be better than 0.6 μm but decreased as a result of the averaging procedures described below to values of approximately 1 μm, depending on the lateral homogeneity of the sample.

To improve the signal-to-noise ratio, each horizontal line (along *x*) of a frame was scanned four times and averaged. Three of these frames were averaged, giving an effective average over 12 measurements per data point. The time needed for one of these cross-sectional images was approximately 5 s. To prevent the samples from premature and irreproducible photobleaching, a "fresh", previously unscanned area of the membrane was chosen for each image.

For each *x*-coordinate, a transversal profile (along *z*) was calculated from the detected fluorescence intensities. Because the membranes were laterally homogeneous (within the *x*,*y* planes), the signal-to-noise ratio was further improved significantly by averaging all transversal profiles for each *x*-coordinate of one frame, albeit the transversal resolution slightly decreased.

For semiquantitative evaluation and comparison of the data, a linear response of the photomultipliers was assumed and a linear baseline was subtracted from all intensity profiles to remove the influence of scattering and dark currents of the photomultiplier. Finally, to account for optical absorption as well as scattering due to inhomogeneities in the grafted membranes (micro-phase separation) by the part of the sample that the excitation light had to pass, a numerical correction according to the Lambert−Beer law was applied to yield symmetric intensity profiles. For that correction, the intensity values were multiplied by a factor obtained recursively from a numerical integration of the profile. The necessary effective absorption coefficient was determined from the additional condition of equal intensities at both surfaces of the membranes.

Results and Discussion

Reflection Mode. Using the *z*-scanning stage of the microscope allowed the sample preparation to be kept as simple as possible. Typical images taken in reflection mode are shown in Figure 1.

Except for inverting for better reproduction and visualization, no image processing or correction was applied. The thin line close to the lower edge of the two frames on the left results from the interface between the cover slip and the water around the membrane sample. This line was used to determine the axial resolution of the optics (<0.6 μm). The reflection images mirror the graft polymer content by showing inhomogeneities or some granularity, especially toward the surfaces of the membrane, and are similar to micrographs of grafted membranes in refs 31 and 32. These inhomogeneities show local variations of the refractive index due to local changes of composition. This indicates at least partial demixing or micro-phase separation of the two polymer components. It has to be pointed out that the structure visible is not an image of the micro-phases. The sizes of the inhomogeneities created by local demixing have to be by far smaller than the optical resolution of the microscope (∼0.2 μm).

The decrease of overall intensity of the reflected light along the cross section from bottom to top shows the decrease of incident light due to absorption and scattering. With increasing degree of grafting from left to right in Figure 1, an

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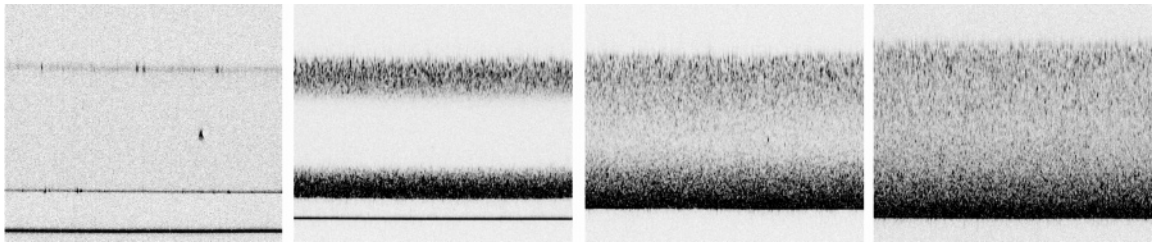

Figure 1. Reflection images (cross sections of the membranes): ETFE-*graft*-poly(styrene), 1%, 16.7%, 35.1%, and 42.2% mass content of poly(styrene) (left to right). The brightness values are inverted for better visualization, illumination from below.

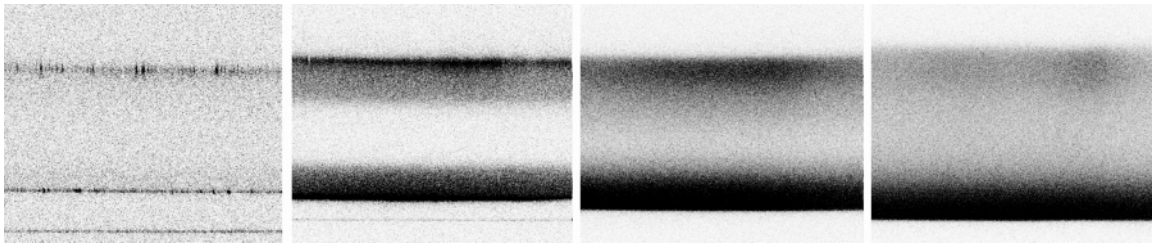

Figure 2. Fluorescence images (cross sections of the membranes): ETFE-*graft*-poly(styrene), 1%, 16.7%, 35.1%, and 42.2% mass content of poly(styrene) (left to right). The brightness values are inverted for better visualization, illumination from below.

increase in thickness of the membranes can also be seen, corresponding to the additional amount of graft polymer.

Fluorescence Mode. Figure 2 gives the corresponding fluorescence images of the same membranes as in Figure 1.

The images in Figure 2 clearly reveal a minimal fluorescence intensity at the centers of the membranes. The first membrane containing only 1% of graft polymer, as determined by gravimetric measurements, nearly shows no fluorescence within the membrane at all. From this, it can be directly concluded that the matrix polymer does not take up any fluorescent dye and does not show intrinsic fluorescence, as expected for the fluorinated polymers used as starting material. This result was verified by staining experiments with pure, ungrafted ETFE and FEP matrix films, that showed no fluorescence even after 48 h hours of exposure to the staining solution. Hence, rubrene proved a suitable dye for selectively staining the parts of the sample containing graft polymer.

Where desired, the added dye can be extracted from the membrane afterward (e.g., with toluene in the case of rubrene). Because the conditions for the extraction procedures are comparable to the conditions when removing residual monomer from the membranes after synthesis, the membrane can be considered unchanged by the CLSM measurements and can be recovered for use.

In comparison to the reflection images, the fluorescence variation through the sample is smoother and less granular. The remaining granularity of the images is essentially a result of detector noise. The dye concentrations within the membranes have to be low to avoid concentration effects on the fluorescence efficiency. Therefore, the concentration of the rubrene solution for staining the membranes was chosen to be 20 mg L^{-1}. This apparently results in sufficiently low concentrations within the membranes. The corresponding low fluorescence intensity has to be detected with high amplification, resulting in a lower signal-to-noise ratio. The signal-to-noise ratio is significantly improved by the averaging procedure described above. However, averaging more than four times proved useless, because rubrene is highly susceptible to photobleaching.[33] Moreover, determination of the absolute content of dye within the membranes, according to the Lambert−Beer law of the fluorescence intensity, has proven to be impossible as a result of this photobleaching effect during the measurements.

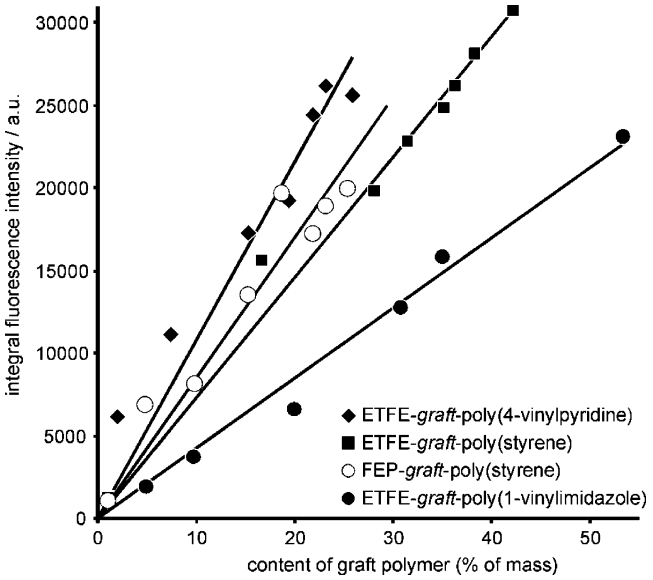

Figure 3. Correlations between mass content of graft polymer and integral fluorescence intensity for ETFE-*graft*-P4VP, ETFE-*graft*-poly(styrene), FEP-*graft*-poly(styrene), and ETFE-*graft*-P1VIm.

To clarify whether the measured fluorescence intensity of the stained membranes is proportional to the content of graft polymer, the integral of the fluorescence intensity taken over the thickness of the sample is plotted against the content of graft polymer as obtained from gravimetric measurements. The results are shown in Figure 3.

From this diagram, a good linear dependence is found for all membranes, especially for higher degrees of grafting. Toward lower concentrations, some deviations from the linear behavior can be observed. Because it is rather difficult

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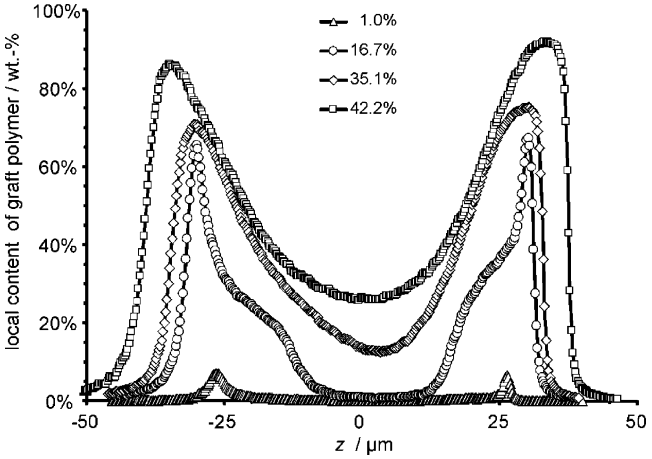

Figure 4. Series of profiles of ETFE-*graft*-poly(styrene) (1%, 16.7%, 35.1%, 42.2% mass content of graft polymer), dyed with rubrene. The depth coordinate *z* is given relative to the center of the membrane.

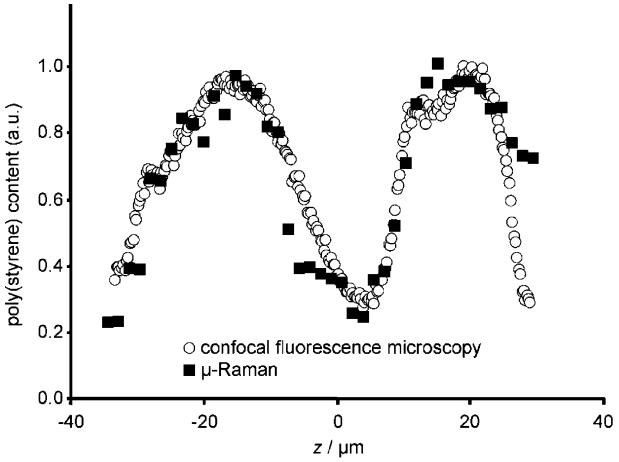

Figure 5. Comparison of profiles showing the local graft polymer content for a ETFE-*graft*-poly(styrene) sample with 17.3 wt % of grafted poly(styrene), obtained by confocal fluorescence microscopy (open circles) and by micro-Raman spectroscopy (black squares).

to stop the reaction after a precisely known short time of grafting to produce membranes with very low content of graft polymer, no more data was available for low concentrations from our reactions. It therefore remains to be clarified with further investigations in the low-graft regime whether these deviations are caused by greater experimental errors or reflect a real, physical non-proportionality. This non-proportionality would generally occur in cases when the polymer components *do not* micro-phase separate, that is, when the assumptions given above are not satisfied. This is supported by the first reflection image in Figure 1, without pronounced scattering from micro-phase interfaces. In a homogeneous mixed phase the fluorescence intensity cannot necessarily been taken as a measure of composition.

To obtain quantitative, spatially resolved concentration profiles of the cross sections, the overall content of graft polymer as measured gravimetrically was used to re-scale the relative fluorescence intensity to the percentage of graft polymer. Because the effect of photobleaching was different for each image, the scaling factors varied from image to image. The profiles showing the local content of graft polymer with increasing grafting time, for the same membranes as depicted in Figures 1 and 2, are given in Figure 4.

For short reaction times only thin layers of graft polymer are formed on the surface of the membrane. With increasing reaction time, the graft reaction proceeds toward the center of the film. Because of the averaging procedure of the acquired images, the resulting profiles appear smooth with a high signal-to-noise ratio. The total acquisition time of the images required for each profile is less than 10 s, and the resolution of the profiles after the averaging routine is about 1 μm.

The concentration profiles obtained by the presented CLSM imaging routine and their evolutions with reaction time are in good agreement with the well-known front mechanism.[34−41] The profiles were also compared to the more established profiling technique via micro-Raman spectroscopy. Such a comparison is illustrated in Figure 5 for a ETFE-*graft*-poly(styrene) sample with 17.3 wt % of grafted poly(styrene).

The comparison shows a good agreement of both methods. The CLSM profile is somewhat smoother due to the averaging of several individual profiles: typically more than 100 lines per frame could be averaged without loss in spatial resolution. This decreased the noise level by about 1 order of magnitude. The Raman results represent a single section of the sample only. Although the membranes were rather homogeneous laterally, a single cross section apparently shows some local concentration variations. Averaging several Raman profiles is an extremely time-consuming task, because a single Raman profile takes, depending on the spatial intervals of the data points, about 1 h. A profile obtained by Raman microscopy with a comparable level of averaging (∼100 individual sections) thus would take days of measuring time.

Compared to FTIR-PAS techniques, the optical resolution of a confocal microscope easily compares to the best resolutions achieved with PAS (∼1−2 μm).[25−27] When electron microscopy combined with EDS is employed to obtain graft profiles, extremely high spatial resolution in the 10 nm range can be achieved. However, sample preparation poses a complicated procedure as flat sections of the membrane samples have to be prepared. Also, EDS is usually used to map the distribution of "heavy" elements like sulfur. Typically, "light" elements (C, O) are the main components of organic polymers, giving poor contrast between two polymers of similar empirical composition and requiring high-resolution X-ray spectrometers.

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Conclusions

In this paper, confocal fluorescence microscopy is presented as a convenient and fast imaging technique for obtaining depth profiles of graft copolymers: compared to established methods the spatial resolution is better than, for example, FTIR-PAS; the measuring time is orders of magnitudes shorter than with micro-Raman profiling, comparing data of equal signal-to-noise ratios; and the sample preparation is simpler than for electron microscopy (if necessary at all). If one of the polymer components is intrinsically fluorescent, no sample preparation is necessary at all, though the size of samples might be limited by the optical setup of the microscope. If none of the components is inherently fluorescent in the accessible spectral range, it is possible to choose a fluorescent dye that selectively stains one of the components. Because the added dye, where required, could also be removed by extraction, this method can be considered to be nondestructive.

As a result of optical absorption and light scattering in the sample as well as bleaching of the fluorescent dyes, it is not generally possible to use the method to measure the graft polymer content on an absolute scale. Additional measurements for calibrating the obtained data are necessary. A simple gravimetric determination of the overall graft polymer content is sufficient.

Although the applied confocal laser microscope greatly facilitates imaging of cross sections of films in principle, a standard fluorescence microscope equipped with an imaging device could be used as well at the cost of more complicated sample preparation. In this case, physical cross sections of the films had to be prepared, for example, as microtome cuts.

The influence of different reaction parameters (e.g., monomer concentration or temperature) on the homogeneity and uniformity of the grafting reaction and a quantitative description of the imaged depth profiles, for example, by introduction of a uniformity parameter, is the subject of current work.

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