Fe^{2+} Catalyzed Synthesis of Radiation Grafted Functional Membranes and Application in Fuel Cells and Ion Recovery

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Summary: 1-Vinylimidazole is grafted onto Poly(ethylene-*alt*-tetrafluoroethylen (ETFE) by means of pre-irradiation technique with electron beam doses between 50 and 150 kGy. The degree of grafting is significantly increased to values of up to 115% by addition of 20-50 mmol/L of an Fe^{2+} salt that facilitates the decomposition of the peroxide structures within the irradiated films. The obtained mechanically stable and flexible ETFE-*graft*-poly(1-vinylimidazole) membranes exhibit a homogenous distribution of the graft polymer for degrees of grafting greater than 50 wt.-% and show thermal stability up to 250 °C. The applicability of these membranes as anhydrous proton conducting material when doped with phosphoric acid and the complexation capability for Cu^{2+} ions is demonstrated.

Keywords: 1-vinylimidazole; electron beam irradiation; ETFE; graft copolymers; membranes

Introduction

Polymeric material bearing imidazole functionalities exhibit interesting properties due to the basicity as well as the nucleophilicity of the N-based heterocycle. Making use of these properties, applications of poly(1-vinylimidazole) (P1VIm, Figure 1, left) include the absorption of heavy metal ions (like Hg^{2+} or Cu^{2+}) by complexation[1] or the binding of acids from aqueous solutions in waste water treatment.[2]

Moreover, considering the imidazole's amphoteric character and the ability to undergo a certain degree of protolytic self-dissociation and formation of an H-bond network, poly(4-vinylimidazole) doped with phosphoric acid has also been presented as a water-free proton conducting material for fuel cells.[3]

Production of self-sustaining insoluble membranes functionalized with imidazole groups can be carried out by radiation-induced graft polymerization of the monomer 1-vinylimidazole onto stable, inert polymer films and has been reported for poly(hexafluoropropylene-*co*-tetrafluoroethylene) (FEP),[4] poly(vinyl alcohol),[5] polyethylene[6] and polypropylene[7] substrates. For a review on radiation grafting, various substrates and functional monomers see.[8]

In this work, we present the radiation-induced grafting of 1-vinylimidazole onto pre-irradiated films of poly(ethylene-*alt*-tetrafluoroethylene) (ETFE, Figure 1, right) and the effect of the addition of an Fe^{2+} salt to the reaction mixture that distinctly increases the degree of grafting and consequently also the homogeneity of the graft polymer's distribution in the ETFE matrix. The obtained ETFE-*graft*-poly(1-vinylimidazole) membranes are characterized and two possible applications, as anhydrous proton conductor after

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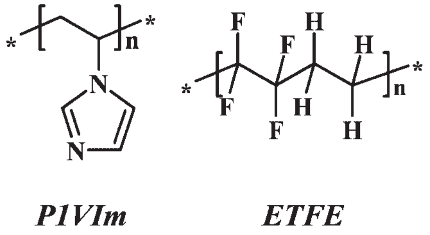

Figure 1.
Poly(1-vinylimidazole) (P1VIm) and poly(ethylene-*alt*-tetrafluoroethylene) (ETFE).

doping with phosphoric acid and as binding material for Cu^{2+} ions, are outlined.

Experimental Part

Materials

ETFE films were obtained in 50 μm thickness from Nowofol GmbH (Germany), 1VIm was purchased from FLUKA and distilled under vacuum before use. $FeSO_4 \times 7\,H_2O$ and phosphoric acid (85 wt.-%, p.a.) were obtained from MERCK.

Graft Polymerization

The method of film irradiation and the general routine for the graft reaction is described elsewhere.[9,10] For this work, graft reactions onto ETFE films activated under air atmosphere by an electron beam with doses of 50, 100 and 150 kGy were carried out in glass ampoules (10 mL) in an agitated thermostat block that was set to 60 °C. The activated ETFE films were immersed in the reaction mixtures (1VIm and water in various ratios) after previously deoxygenating the solutions by passing nitrogen gas for 20 minutes. After the desired reaction time, the membranes were taken out and residual monomer was extracted by methanol. To remove iron side products, the membranes were treated with diluted hydrochloric acid (0,1 mol/L) for 24 h and then washed acid free with water. After drying the products, the degree of grafting (*d.o.g.*) is determined as the relative weight increase in percent (*d.o.g.* = 100 × mass of grafted P1VIm/mass of ETFE film before reaction). Functional density (ρ) of the imidazole groups in ETFE-*graft*-poly(1-vinylimidazole) can be calculated from the *d.o.g.* via Equation (1).

$$\rho(\mathrm{mmol/g}) = \frac{\frac{d.o.g.}{100}}{0.09412\,\frac{\mathrm{g}}{\mathrm{mmol}} \times \left(1 + \frac{d.o.g.}{100}\right)} \qquad (1)$$

Results and Discussion

Synthesis of ETFE-*graft*-poly(1-vinylimidazole)

When employing the pre-irradiation grafting technique of 1-vinylimidazole onto ETFE films it turns out that achievable degrees of grafting are not very well reproducible and vary greatly between 0% and about 30%. However, when adding Fe^{2+} ions to the reaction mixture in the form of $FeSO_4 \times 7\,H_2O$ not only the reproducibility but also the degree of grafting is significantly increased as demonstrated in Figure 2 for a set of three ETFE films irradiated with 50, 100 and 150 kGy.

With an optimal concentration between 20 and 50 mmol/L, degrees of grafting between 50% and 115%, depending on the irradiation dose used, can be achieved. The reason for this distinct increase upon iron salt addition is probably the enhanced

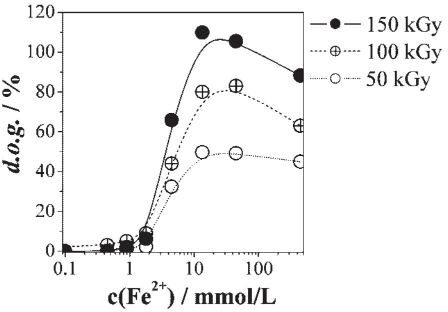

Figure 2.
Degree of grafting (*d.o.g.*) for grafting of 1VIm onto ETFE as a function of the Fe^{2+} concentration in the reaction mixture (60 °C, 87.5 vol-% 1VIm in water, after 72 h).

decomposition rate of peroxide structures that are formed when the base film is irradiated under air ($P–O–O–H + Fe^{2+} \rightarrow P–O\cdot + OH^- + Fe^{3+}$) that consequently leads to a higher grafting rate. In other publications, Fe^{2+} has mainly been applied to reduce the homopolymerization rate of the monomer in simultaneous radiation-grafting techniques and for some systems addition of inorganic salts also results in a salting in/out effect between the monomer and the polymer phase.[8,11] In this case, these effects do not contribute significantly to the observed increase in the degree of grafting and to our knowlegde such distinct effect has not yet been reported for pre-irradiation grafting.

The effect of the variation of two other reaction parameters, volume fraction of the monomer in aqueous solution (ϕ) and reaction time, is displayed in Figure 3. Concerning the reaction temperature, performing the reactions at 60 °C produces the best results.

Degree of grafting is only increased to a small extent when increasing the monomer volume fraction to about 60 vol-% but rises steeply for higher monomer contents with a maximum at 88 vol-%. For higher volume fractions, *d.o.g.* is reduced again due to the limited solubility of the Fe^{2+} additive in reaction mixtures with low water content. The grafting process itself is still quite slow and is essentially finished after ca. 12 h of reaction time with the degree of grafting only progressing very slowly for longer durations. For details and peculiarities of the radical polymerization of 1-vinylimidazole causing such a low polymerization rate see.[12]

The obtained ETFE-*graft*-poly(1-vinylimidazole) membranes bear a functional density of the imidazole groups of $\rho =$ 5,68 mmol/g in the case of the highest *d.o.g.* of 115% and turn out to be mechanically stable and robust even when high doses of 150 kGy were previously applied for activation. Thermogravimetric measurements under air (TGA 850 Mettler Toledo, heating rate of 20 K/min) show two distinct decomposition steps beginning at 290 °C for the degradation of the grafted P1VIm and at 450 °C for the ETFE matrix providing long-term thermal stability of the material for temperatures of up to 250 °C.

The homogeneity of the graft polymer's distribution within the matrix (''graft profile'') can be probed by measurements of the fluorescence intensity since the grafted P1VIm, in contrast to the inactive ETFE matrix, exhibits intrinsic fluoresence. For

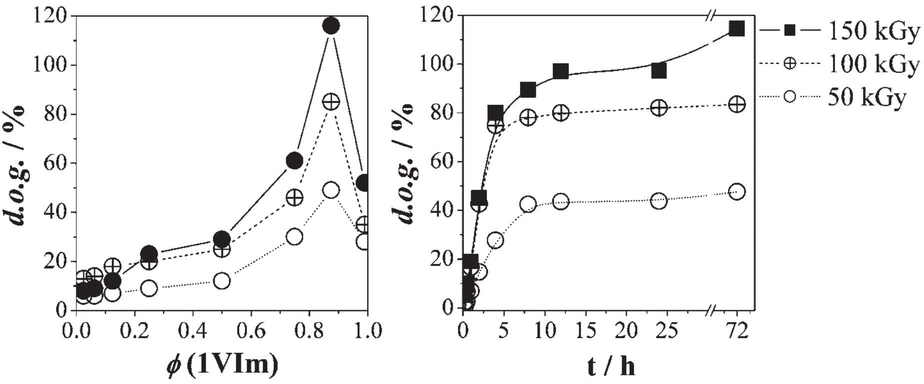

Figure 3.
Degree of grafting (*d.o.g.*) for grafting of 1VIm onto ETFE as a function of the volume fraction of monomer in water (ϕ) (60 °C, 50 mmol/L Fe^{2+}, after 72 h, left) and as a function of the reaction time (t) (60 °C, 50 mmol/L Fe^{2+}, 87.5 vol-% 1VIm in water, after 72 h, right).

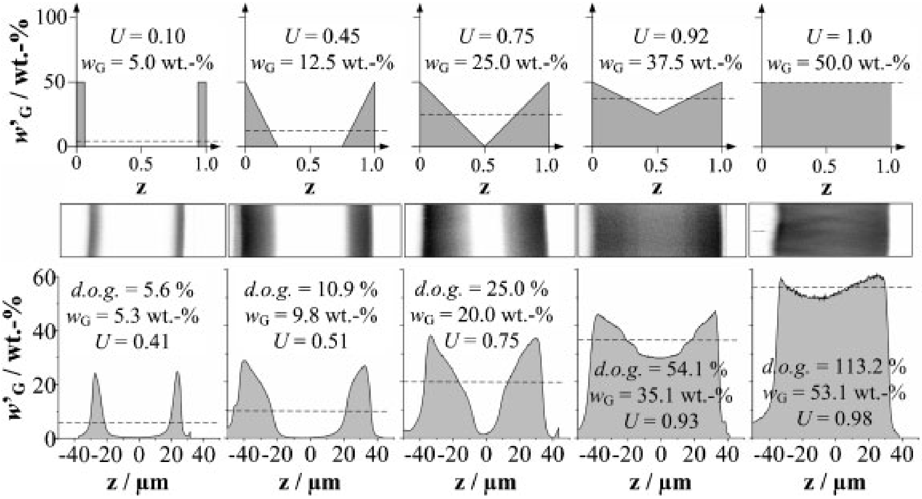

Figure 4.
Abstract graft profiles and corresponding *U*-parameters (above), fluorescence images (middle) and derived profiles (below) for ETFE-*graft*-poly(1-vinylimidazole) samples with z: depth coordinate (cross-section of membrane), w'_G: local mass content of P1VIm at z and dotted line: average mass content of P1VIm in membrane (w_G).

mapping the local mass content of the graft polymer (w'_G) along the z-axis, i.e. following the cross section of a membrane sample, a confocal laser scanning microscope (CLSM) with fluoerescene detection was applied, the according method and set-up have been described in detail by us in.[13] For a simple evaluation of the uniformity of the profiles obtained by this method, we introduce a uniformity-parameter U that ranges from 0 for grafting that only occurs at the surface of the films to 1.0 for ideal, rectangular distribution of the graft polymer through the membrane's cross-section. This parameter is calculated over n data points of the profile from the local graft polymer's mass content at the given z-coordinate ($w'_G(z)$) and the overall mass content of the graft polymer (w_G, mass of grafted P1VIm alone divided by total mass of membrane or *d.o.g.*/(*d.o.g.*+100)) (see Equation (2)).

$$U = 1 - \frac{\sum_{i=1}^{n} \left| w'_G(z) - w_G \right|}{2 \cdot n \cdot w_G} \qquad (2)$$

Figure 4 comprises some abstract profiles and the corresponding derived U-parameters for illustration and provides fluorescence images, resulting profiles and uniformity values for ETFE-*graft*-poly(1-vinylimidazole) membrane samples with increasing *d.o.g*.

For the given graft reaction, a homogeneous distribution along the membrane's cross-section is achieved for degrees of grafting higher than 50%. When aiming at applications that rely upon a transversal transport through the membrane, like proton transport in fuel cell membranes, a homogeneous distribution of the functional graft polymer is of major importance and a corresponding U-parameter of roughly 0.9, that can be obtained by allowing a corresponding minimal degree of grafting, is therefore advised. The sequence of the presented real profiles and their accordance to the theoretical profiles in Figure 4 also represents an illustrative example of the front-mechanism of graft reactions with the grafting fronts starting at the surface, then growing inwards and eventually meeting and overlapping in the center.[8]

Application of ETFE-*graft*-poly(1-vinylimidazole) as Proton Conductor

Composites of basic polymers (like poly(benzimidazole)) and phosphoric acid have been presented as a promising approach to anhydrous proton conducting material that circumvents the problems of water-based proton conductors, like limited operation temperatures or a complicated water management system for humidification.[3,14]

Making use of the basicity introduced upon grafting with 1-vinylimidazole, the produced membranes can be doped with phosphoric acid adapting a literature procedure presented for poly(benzimidazole) (PBI) as matrix.[15] Doing so, a basic polymer-phosphoric acid-composite can be obtained that contains up to 70 wt.-% of the dopant acid equaling an acid concentration of 12.5 mol/L within the membrane or 4.2 molecules of phosphoric acid per imidazole group. The dopant phosphoric acid introduces high hydrophilicity into the material and acts as a strong plasticizer for the membranes that become softer and more flexible but still retain a high mechanical strength even for highest doping grades due to the internal stabilization from the ETFE matrix (E-modulus = 30 MPa and elongation at break = 105% for 70 wt.-% acid, according to stress-strain experiments at 20 °C with 10 mm/min). The specific proton conductivities (σ) of these membranes can be determined via two-point eletrochemical impedance spectroscopy following a typical set-up and routine presented in.[14] The measurements were conducted in dry air without additional humidification in the temperature range from 20 °C to 120 °C after drying and conditioning the membrane for 1 h in the cell. The results for various acid contents in the membrane are shown in Figure 5.

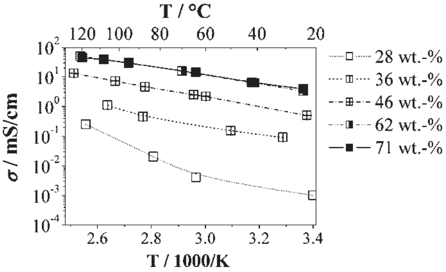

Figure 5.

Specific proton conductivities (σ) for ETFE-*graft*-poly(1-vinylimidazole) membranes doped with various amounts of phosphoric acid (wt.-% given in diagram). Measurements were conducted in dry air.

Achievable proton conductivities strongly increase with dopant concentration as the average distance between two dopant molecules is reduced and therefore the probability of a proton tunneling step, that is mainly responsible for the proton conduction via structure diffusion, is increased.[16] When reaching the saturation amount of acid content (ca. 60 wt.-% in this case), no further increase in conductivity is observed. The conductivity also increases with temperature and reaches high values up to 50 mS/cm for 120 °C in dry air in case of highly doped membranes.

Main advantage of this novel material compared to established reference systems, like phosphorous acid doped PBI, is the increased mechanical stability of these membranes even at high doping levels which facilitates processing of the obtained products (like hot-pressing to membrane-electrode-assemblies). The effective acid concentration within the composite membranes (12 to 14 mol/L of phosphoric acid) and the performance in electrochemical impedance spectroscopy (~100 mS/cm at 190 °C for doped PBI) are comparable to that reference,[17] while most other publications dealing with acid doped polymers as proton conductors have either resulted in poor conductivities or polymer gels that hardly form stable, self-sustaining membranes.[3] Preliminary tests in fuel cells at 120 °C with dry H_2/O_2 at 3 bar provided a current density of 160 mA/cm^2 and a principal proof of the concept (compared to 220 mA/cm^2 for doped PBI at 120 °C, 1 bar H_2 pressure in dry atmosphere[18]).

Application of ETFE-*graft*-poly(1-vinylimidazole) for Cu^{2+} Recovery

Homopolymers of P1VIm have already been investigated for their ability to effectively bind Cu^{2+} ions from aqueous solutions.[1] Combining this complexing capability of the imidazole groups with the graft polymerization onto an insoluble, inert backbone polymer membrane provides an easy-to-use and re-usable seperation membrane. Preliminary studies show that for ensuring an effective absorption of Cu^{2+} ions from aqueous solutions, the degree of grafting has to be as high as possible to reduce the impact of the hydrophobic ETFE backbone and to increase the membrane' swelling and thus the accesibility of the imidazole groups in the membrane. Coordination number of poly(1-vinylimidazole)-Cu^{2+}-complexes in solution is reported to be 4,[19] while in the case of ETFE-*graft*-poly(1-vinylimidazole) membranes with their sterically more hindered functions, a maximum uptake ratio of 4.5 imidazole to 1 Cu^{2+} ion has been observed resulting in an effective uptake capacity for Cu^{2+} of 1.25 mmol/g (~79 mg/g) for membranes with a *d.o.g.* of 115%. In addition, the counter anion of the copper salt and 3 to 4 water molecules per Cu^{2+} ion are also incorporated. After absorption, Cu^{2+} can be quantitatively extracted from the membranes by sulfuric acid (0.1 mol/L, 15 min, 20 °C) and the membranes can be re-used after washing them acid free. Compared to the non-membrane bound poly(1-vinylimidazole) with a functional density of 10.6 mmol/g and a uptake capacity of 2.66 mmol/g (~169 mg/g)[19] performance is reduced for the sake of much easier handling and processing when employing the non-soluble graft polymer membrane.

Conclusion

ETFE-*graft*-poly(1-vinylimidazole) membranes can be produced in high degrees of grafting (115%) and with high functional densities (5,69 mmol/g) by grafting 1-vinylimidazole onto previously irradiated ETFE films (50–150 kGy) at 60 °C from an aqueous reaction mixture containing 50 mmol/L of Fe^{2+} and ~88 vol-% of the monomer. For obtaining a homogeneous distribution of the graft polymer throughout the membrane, a minimal degree of grafting of 50% has to be ensured. The functional membranes are mechanically robust and exhibit thermal stability for temperatures up to 250 °C. Composites of these membranes with 70 wt.-% phosphoric acid show high proton conductivities of 50 mS/cm at 120 °C without additional humidification and seem promising for an application as anhydrous proton conducting material though long-term stability tests are still underway. The complexing nature of the imidazole functions also allows the use of these membranes as easy-to-use and re-usable binding material for Cu^{2+} ions with a capacity of up to 79 mg/g.

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