

Preparation of polymer electrolyte membranes for lithium batteries by radiation-induced graft copolymerization

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Abstract

Polymer electrolyte membranes with different degrees of grafting were prepared by radiation-induced graft copolymerization of styrene monomer onto poly(vinylidene fluoride) (PVDF) films and subsequent chemical activation with liquid electrolyte consisting of lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate/diethylene carbonate (EC/DEC). The chemical changes in the PVDF films after styrene grafting and subsequent chemical activation were monitored by FTIR spectroscopic analysis and the crystallinity was evaluated using differential scanning calorimetric (DSC) analysis. The swelling in electrolyte solution (electrolyte uptake) and the ionic conductivity of the membranes were determined at various degrees of grafting. The conductivity of the membranes was found to increase with the increase in the degree of grafting and reached a magnitude of 10⁻³ S/cm at a degree of grafting of 50%. The results of this work suggest that radiation-induced graft polymerization provides an alternative method to substitute blending in preparation of polymer electrolyte membranes for application in lithium batteries.

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1. Introduction

Polymer electrolyte membranes are a class of materials that is attracting ever-increasing interest in the industry and academe due to their applicability for a variety of solid-state and electrochemical device applications including batteries, fuel cells, super capacitors and chemical sensors [1,2]. After the successful technical feasibility study conducted by Armand et al., polymer electrolytes started to play an important role in developing new types of rechargeable lithium or lithium-ion batteries [3,4]. However, most of the all-solid-state polymer electrolytes (SPE) have low ionic conductivities (less than 10⁻⁵ S/cm at room temperature) as a result of the low mobility of the charge carriers in the polymer matrices. This magnitude of conductivity is far from the adequate level for practical room temperature applications. To improve the ionic conductivity, a liquid solution of a lithium salt containing aprotic polar solvents such as

ethylene carbonate (EC) and dimethylene carbonate (DEC) is hosted in polymer matrices resulting in gel-type polymer electrolytes having ionic conductivities of the order of 10⁻³ S/cm at room temperature, almost as high as that of liquid electrolytes [5,6].

Various polymer matrices, such as polyacrylonitrile [7] poly(vinyl chloride) [8] poly(methyl methacrylate) [9,10], poly(vinyl sulfone) [11] and poly(vinylidene fluoride) [12,13], have been used to host the liquid electrolyte. Among all, poly(vinylidene fluoride) (PVDF) is the one that has been most widely studied in preparation of polymer electrolyte membranes due its appealing properties [14–20]. The PVDF matrix is often modified by copolymerization with monomers such as hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE) or styrene to reduce the crystallinity and to help generating amorphous domains in an otherwise predominantly crystalline PVDF structure [21,22]. The liquid electrolyte component is present almost exclusively in such amorphous domains of the polymer matrix; the microcrystalline regions serve as physical cross-links providing the necessary mechanical strength [8]. However, most PVDF-based modifications

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carried out thus far were performed through blending technology, in which the miscibility between different polymers is limited to the macroscopic level.

Radiation-induced graft copolymerization offers an alternative method to combine two highly incompatible polymers and retain the desirable properties of the two polymeric components. This method has been used to prepare polymer electrolyte membranes suitable for uses in fuel cells [23], water electrolyzers [24], batteries [25] and sensors [26]. The attractive features of the graft copolymerization process is that the amount of grafted component can be easily controlled by the proper selection of reaction parameters. As a result, polymer electrolyte membranes with desired physico-chemical properties can be tailored. In this paper, we report on the preparation and characterization of gel-type polymer electrolyte membrane for lithium batteries by radiation-induced graft copolymerization of styrene monomer onto PVDF film and subsequent chemical activation with lithium hexafluorophosphate (LiPF₆)/EC/DEC liquid electrolyte mixture. Some of the obtained electrolyte properties are investigated in correlation with the amount of polystyrene grafted therein, i.e., the degree of grafting.

2. Experimental

2.1. Materials

PVDF film of 80- μ m thickness and density of 1.76 cm³/g (Goodfellow, UK) was used as a polymer matrix. Styrene of purity more than 99% (Fluka, Switzerland) was used as a grafting monomer without any further purification. The electrolyte solution consisting of a 1.0 M solution of LiPF₆ in a 1:1 w/w EC–DEC mixture was provided by Merck (Selectipur™, H₂O content <50 ppm). All the solvents were reagent grade and used as received.

2.2. Polymer electrolyte membrane preparation

The preparation of the membranes includes a two-step procedure. The first step involves the preparation of a graft copolymer precursor by grafting of styrene onto PVDF film using simultaneous irradiation technique. PVDF film of known weight and dimension was immersed in styrene monomer having known concentration and diluted with toluene hosted in a glass ampoule. The solution was flushed with purified nitrogen to remove air and irradiated using γ -rays from a Co-60 source to a maximum total dose of 30 kGy at a dose rate of 0.37 Gy/s at room temperature. After grafting completion, the grafted film was removed, washed thoroughly with toluene several times and soaked therein for 16 h to completely eliminate the homopolymer and the unreacted monomer occluded to the surface of the film. The clean grafted film was finally dried under vacuum, weighed,

and its dimensions were measured. The degree of grafting (Y) was calculated using the following equation:

$$Y\% = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where, W_g and W_0 are the weights of grafted and original (pre-grafted) PVDF films, respectively. In the second step, the polystyrene-grafted PVDF (PVDF-g-PS) precursor were activated by loading with the liquid electrolyte mixture. To enhance the electrolyte uptake, PVDF-g-PS films were initially swollen in plasticizer solvent (DMF) for a few hours; then the solvent was evaporated by drying in a vacuum oven at 60 °C for 24 h. Subsequently, the grafted films were transferred to an M-Braun recirculating Ar glove box where both moisture and oxygen levels were kept below 1 ppm each at 70 °C. The grafted films were immersed in 1 M LiPF₆ in a 1:1 (v/v) mixture EC and DEC, a common electrolyte for lithium-ion batteries, until equilibrium weight was achieved. The impregnated polymer membranes were then stored in a tightly sealed vial in the glove box.

2.3. FTIR measurements

FTIR analysis was conducted using a Perkin Elmer (Spectrum 2000 Explorer) spectrophotometer at ambient conditions. The spectra were obtained in the absorbance mode in a wave number range of 4000–500 cm⁻¹ and analysed using commercial software. Samples of original PVDF and PVDF-g-PS films were used as reference materials.

2.4. DSC measurements

Differential scanning calorimetry (DSC) thermograms of the polymer electrolyte membranes were measured with a Perkin-Elmer DSC-7 (Pyris 1) calorimeter at heating rate of 10 min⁻¹ under nitrogen atmosphere and in a temperature range of 50–400 °C. All membrane samples were sealed in a glove box into aluminum pans prior DSC runs. Thermograms were obtained from the first heating run. Original PVDF and PVDF-g-PS films were used as references. The degree of crystallinity (X_c) in the original PVDF film was directly calculated using Eq. (2).

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100 \quad (2)$$

where, ΔH_m is the heat of melting of PVDF film obtained from the peak area and ΔH_{m100} is the heat of melting of 100% crystalline PVDF polymer, which equals 104.7 J/g [27].

Since the incorporated polystyrene has an amorphous nature, the crystallinity of the PVDF-g-PS and that of the final electrolyte membranes is always referred to the fraction of PVDF matrix. The degree of crystallinity of PVDF-g-PS films is calculated using Eq. (2) after correcting the recorded

ΔH_m by dividing over the weight fraction of PVDF in the grafted film (W_{PVDF}), which is obtained from Eq. (3):

$$W_{\text{PVDF}} = m_{\text{PVDF}} / (m_{\text{PVDF}} + m_{\text{PS}}) \quad (3)$$

where, m_{PVDF} and m_{PS} are the weight fractions of PVDF and grafted polystyrene, respectively. Similarly, the degree of crystallinity of the electrolyte membranes is calculated using Eq. (2) after correcting the recorded ΔH_m by dividing over the weight fraction of PVDF in the electrolyte membranes (W_{PVDF}) which is obtained using Eq. (4):

$$W_{\text{PVDF}} = m_{\text{PVDF}} / (m_{\text{PVDF}} + m_{\text{PS}} + m_{\text{Electrolyte}}) \quad (4)$$

where, $m_{\text{Electrolyte}}$ is weight of the absorbed electrolyte in the membrane.

2.5. Liquid electrolyte uptake

The liquid electrolyte uptake was determined during the membrane preparation. The PVDF-g-PS film was soaked in liquid electrolyte several hours and the equilibrated membrane was removed and the excess electrolyte adhering to its surfaces was blotted using laboratory wipes then quickly weighed. The liquid electrolyte uptake and the porosity (ϵ) of the swollen PVDF-g-PS (electrolyte membrane) were determined from the difference in the weights of dried PVDF-g-PS and its swollen counterpart. The porosity (ϵ) of the electrolyte membranes was calculated using Eq. (5).

$$\begin{aligned} \epsilon &= \frac{\text{liquid electrolyte uptake volume}}{\text{total volume}} \\ &= \frac{(W_s - W_0)\rho_0}{(W_s - W_0)\rho_0 + W_0\rho_{\text{sol}}} \end{aligned} \quad (5)$$

where W_s and W_0 are the weights of electrolyte swollen membranes and dry PVDF-g-PS films, respectively. ρ_0 is the apparent density of dried PVDF-g-PS films which is calculated for every sample by taking the dimensional changes after grafting into account and ρ_{sol} is the liquid electrolyte solution density, which equals 1.22 g/cm^3 at 25°C .

2.6. Ionic conductivity

Ionic conductivity of the polymer electrolyte membranes was measured at room temperature by complex AC impedance spectroscopy. Measurements were carried using frequency response analyser (Autolab PGSTAT 30) at a frequency range of 0.01–100 kHz. Circular samples impregnated with liquid electrolyte were sandwiched between two stainless steel electrodes having round-end discs (20 mm diameter) and hosted into self-made Teflon casing. The ionic conductivity of the polymer electrolyte membranes was calculated from Eq. (6):

$$\sigma = d / (R_b r^2 \pi) \quad (6)$$

where d and r represent, respectively, the thickness and the radius of the sample membrane discs. R_b (bulk resistance) was obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance.

3. Results and discussion

Preparation of the graft copolymer precursor (PVDF-g-PS) was carried out by simultaneous grafting of styrene onto PVDF films. Five samples having various degrees of grafting in the range of 5–50% were obtained under controlled parameters. To exclude the effects of temperature, monomer concentration, dose rate, type of solvent and film thickness, these parameters were kept constant while varying the dose. Fig. 1 shows the relationship between the degree of grafting and the irradiation dose. The degree of grafting increases gradually with the increase in the irradiation dose. This behaviour can be understood based on the fact that the increase in the dose leads to generation of more radicals in the grafting system, and as a result, more radicals contribute to grafting reaction.

To confirm the grafting of styrene in the grafted PVDF films, FTIR spectra was conducted. Fig. 2 shows FTIR spectral analysis of PVDF-g-PS films having various degrees of grafting. Additional characteristic peaks representing polystyrene features compared to original PVDF film can be clearly observed. This includes the benzene ring features: C–H aromatic symmetric stretching vibrations at 3100 and 3025 cm^{-1} and skeletal C=C in plate-stretching vibrations at 1493 and 1602 cm^{-1} , respectively. The presence of aromatic out-of-plane C–H deformation band at 710 cm^{-1} is due to monosubstitution of benzene ring. The size of the characteristic peaks of benzene ring increases with the increase in the degree of grafting.

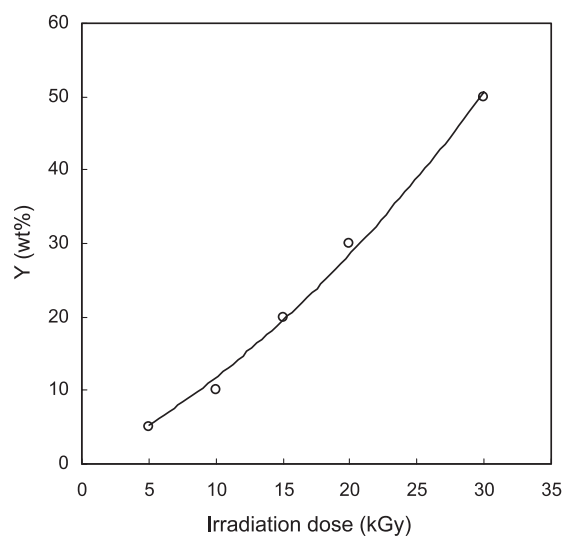


Fig. 1. The degree of grafting in PVDF-g-PS films vs. the irradiation dose.

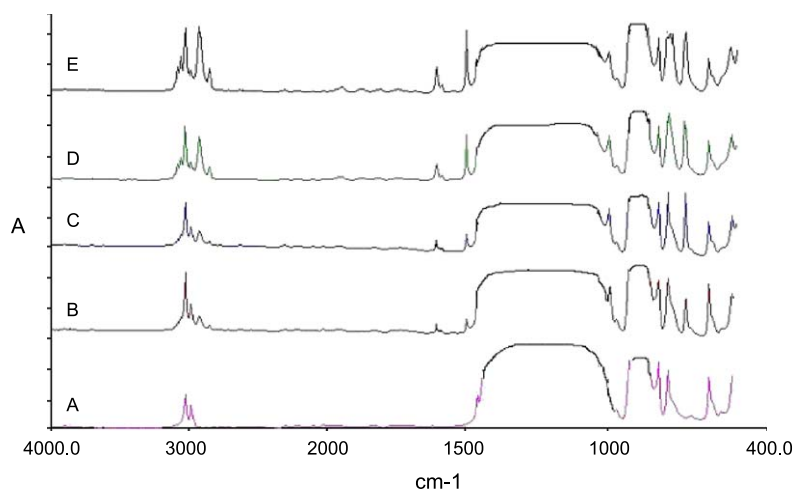


Fig. 2. FTIR spectra of (A) original PVDF film and PVDF-g-PS films having various degrees of grafting: (B) 10%, (C) 20%, (D) 30% and (E) 50%.

After activation of the PVDF-g-PS with the liquid electrolyte, FTIR spectral analysis of the obtained polymer electrolyte membranes were recorded. Fig. 3 shows spectrum of polymer electrolyte membrane having a degree of grafting of 50% compared to unactivated and pre-grafted counterparts. The spectrum of the PVDF-g-PS film activated with $\text{LiPF}_6/\text{EC}/\text{DEC}$ shows characteristic bands of carbonyl groups at $1750\text{--}1800\text{ cm}^{-1}$ that may be attributed to the fragmented and polymerized solvents (EC and DEC), respectively [28,29]. The weak band at 3320 cm^{-1} can be assigned to LiPF_6 [30]. The band at 3550 cm^{-1} is due to the $-\text{OH}$ group which possibly originated from hydration effects.

The changes in the crystalline structure of PVDF films caused by grafting and subsequent activation with the liquid electrolyte is monitored by DSC. Fig. 4 shows typical DSC melting thermograms of 50% PVDF-g-PS film and its activated counterpart. Original PVDF film was used as a reference. The original PVDF recorded a bimodal melting endotherm with melting temperatures, respectively, at 162.6

and $167.9\text{ }^\circ\text{C}$ due to the presence of two lamellae of different thicknesses [31]. The low melting temperature is due to the thinner lamellae of PVDF, whereas the high melting temperature is due to the reorganized thicker lamellae under the influence of heat treatment. The area under the peak of thicker lamellae is noticed to be bigger than that under the thinner one. Grafting of polystyrene was found to alter the shape of the melting peak so that the area under lower melting peak increased while that under the high melting peak decreased indicating that the lamellar growth is inhibited by the formation of polystyrene grafts. The total area under the two peaks is reduced despite the absence of any significant change in the two melting temperatures of PVDF reflecting reduction in the crystallinity. This indicates that styrene did not cause any swelling in the crystallites during grafting, and the formed polystyrene grafts did not penetrate the crystallites of the lamellae despite the formation radicals on their surfaces. This suggests that grafting of polystyrene took place in the entire amorphous region of

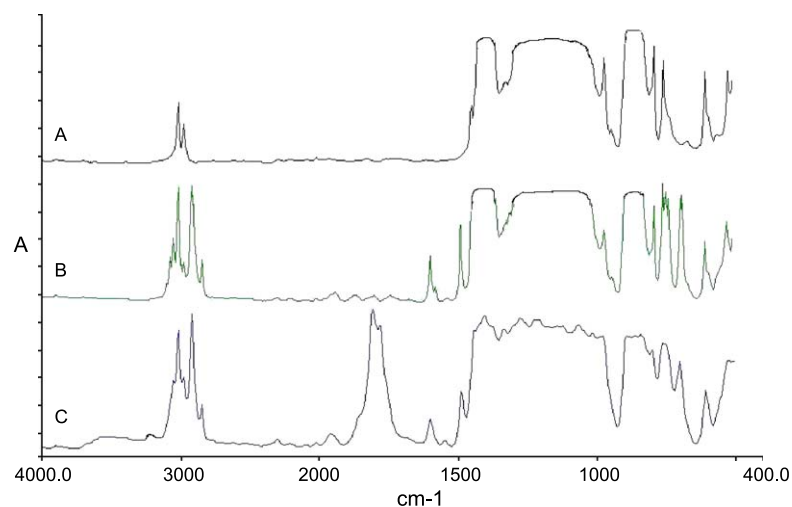


Fig. 3. FTIR Spectra of (A) original PVDF film, (B) PVDF-g-PS and (C) activated polymer electrolyte membrane of 50% degree of grafting.

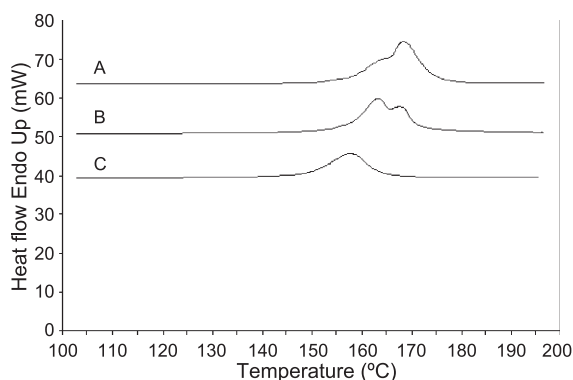


Fig. 4. DSC thermograms of (A) original PVDF film, (B) PVDF-g-PS and (C) activated polymer electrolyte membrane of 50% degree of grafting.

PVDF film and possibly at the surface of the crystallites present at the surface of the lamellae. Therefore, the reduction in the degree of crystallinity, calculated from Eq. (2), from 39.2 to 26.6 upon grafting of styrene ($Y=50\%$) can be attributed to the dilution of the crystalline structure of the PVDF film with the amorphous polystyrene.

Activation of PVDF-g-PS film ($Y=50\%$) with the liquid electrolyte after solvent treatment (plasticization) was found to drastically affect the melting behaviour of the original PVDF film. For instance, the bimodal peak present in the original and grafted PVDF films vanished leaving a single peak with smaller area and lower melting temperature ($157.4\text{ }^{\circ}\text{C}$). The degree of crystallinity (X_c) was found to be suppressed by introducing the liquid electrolyte and reached a value of 21.5%. These observations suggest that post-grafting treatments (plasticization and liquid electrolyte impregnation) induced a crystal disorder in a way that led to a partial distortion in the crystalline order remaining in the PVDF film after styrene grafting. This is possibly due to the strong interaction of the polymer chains with the plasticizer and lithium salts which results in a gel polymer electrolyte of reduced crystallinity. Similar results were reported for PVDF-based gel polymer electrolyte prepared by solvent casting of mixed PVDF with LiBF_4 in EC/PC [32] and

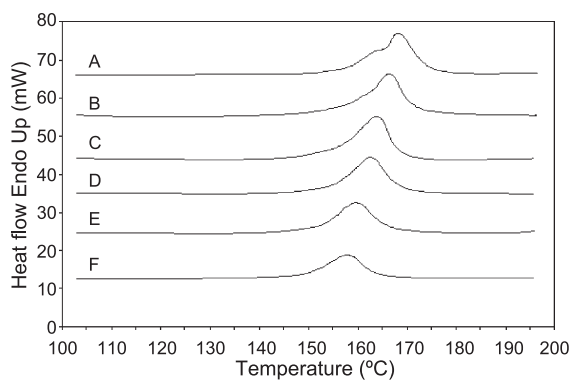


Fig. 5. DSC thermograms of (A) original PVDF film and activated PVDF-g-PS films having various degrees of grafting: (B) 5% (C) 10%, (D) 20%, (E) 30% and (F) 50%.

Table 1

Melting temperature (T_m) and degree of crystallinity (X_c) of polymer electrolyte membranes with various degrees of grafting (Y)

Y (wt.%)	T_m ($^{\circ}\text{C}$)	X_c
0	167.9 ^a	39.2
5	166.7	34.9
10	164.1	30.7
20	162.6	28.2
30	160.0	25.8
50	157.4	21.5

^a Referring to the high melting peak.

another one prepared by complexation of PVDF mixed LiPH_6 with LiPH_6 in EC/PC [33].

To further illustrate the structural changes taking place during the membrane preparation, electrolyte membrane samples having various degrees of grafting were investigated with DSC and the recorded thermograms presented in Fig. 5. The bimodal sharp peak in the original PVDF film was converted to single peaks in the activated membranes, which their peak areas were found varying downward and broadening with the increase in the degree of grafting. Coincidentally, the degree of crystallinity was found to decrease with the increase in the degree of grafting and so does the melting temperature as obviously seen in Table 1. These results suggest the presence of partial crystal disorder in all activated membranes caused by introducing of the liquid electrolyte. However, the level of such disorder varies depending on the degree of grafting, i.e., more disorder occurs at high degree of grafting and vice versa. These results suggest that the reduction in the degree of crystallinity in the activated membranes is not only due to the dilution of the crystalline structure of the PVDF with amorphous polystyrene but also due to the partial disruption caused by impregnation with liquid electrolyte. Such reduction in the crystallinity of the matrix is expected to increase the ionic conductivity of the polymer electrolyte membrane since it is generally known that high conductivity is necessarily associated with an amorphous phase of the polymer [34].

The porosity of the wet membrane obtained from Eq. (5) and the liquid electrolyte uptake (L) defined as the ratio of the mass of electrolyte-swollen PVDF-g-PS films to that of dry PVDF-g-PS film at equilibrium are presented in correlation with the degree of grafting as shown in Table 2. These results show that L increases with the increase in the degree

Table 2

The porosity (ϵ), liquid uptake (L) and thickness (d) of polymer electrolyte membranes with various degrees of grafting (Y)

Y (wt.%)	ϵ	ρ_0 (g cm^{-3})	L (wt.%)	d (μm)
5	0.1211 ± 0.01	1.769 ± 0.01	9.5 ± 0.2	124 ± 1.0
10	0.1667	1.781	13.7	133
20	0.2506	1.797	22.7	145
30	0.2880	1.814	27.2	148
50	0.3918	1.836	42.8	153

of grafting. This was coupled with a parallel increase in the apparent density of the dry PVDF-g-PS film, the porosity of the wet membranes and their thicknesses. The increase in the liquid uptake capacity with the increase in the degree of grafting is due to the suppression of the degree of crystallinity by the dilution with of amorphous polystyrene grafts and the partial disruption in the crystalline structure. This increases of the amorphous domain of the predominantly crystalline PVDF structure and remarkably enhances the swelling of the polymer electrolyte. The simultaneous increase in the porosity and the thickness of the wet membranes with the incorporation of more polystyrene grafts suggests the presence of some microscopic channels formed in the matrices during treatment with the plasticizing solvent. The strong stress of swelling/swelling resistance formed at the interface of the crystallites of PVDF with polystyrene grafts when the latter swells in the plasticizer causes some of the grafted chains to cleave off leaving tiny channels when the solvent removed from the grafted film by drying. This further enhances the liquid electrolyte uptake of the membranes. Therefore, the overall electrolyte uptake in these membranes is governed by swelling of the polystyrene in the amorphous phase and the filling up of the microscopic channels.

It is worth mentioning that the high value of liquid electrolyte uptake ($\sim 43\%$) achieved at $Y=50\%$ makes PVDF-g-PS electrolyte membranes comparable with those based on copolymers of PVDF with HFP, which could absorb 45% of the liquid electrolyte, without the addition of inorganic filler [14].

The dependence of the ionic conductivity on the degree of grafting is shown in Fig. 6. The ionic conductivity of PVDF-g-PS-based polymer electrolyte was found to increase with the increase in the degree of grafting, i.e., the greater the amount of polystyrene grafted therein, the higher the conductivity of the membranes. However, such increase was

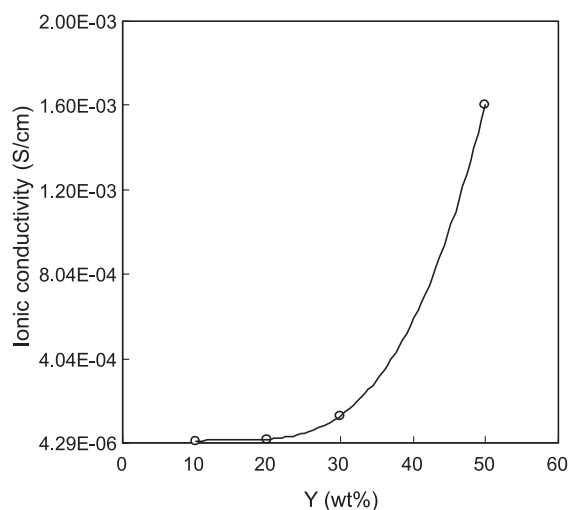


Fig. 6. The ionic conductivity of the polymer electrolyte membranes vs. the degree of grafting.

slow up to 30% degree of grafting beyond which it increases drastically to reach a value of 1.61×10^{-3} S/cm at a degree of grafting of 50%. This value is substantially higher than that of the PVDF-HFP and PVDF-HFP/PS-based polymer electrolyte systems, which equal 0.2×10^{-3} and 0.162×10^{-3} S/cm, respectively [14,20]. This behavior can be generally attributed to the increase in the amorphous content, which trap more liquid electrolyte with the increase in the degree of grafting. However, one should obtain a linear relationship if only amorphous phase swells. To further illustrate this behavior, the mechanism of conduction is taken into account. Grafting of styrene onto fluorinated polymer films (PVDF) forms two-phase separated micro-domain structures due to the difference in the nature of the two components of the grafted PVDF films [35,36]. The presence of such phase separation between PS and PVDF most likely causes the formation of liquid electrolyte-rich polystyrene domains surrounded by crystalline structures. The location of the swollen polystyrene domains and the degree of their possible interconnection depends not only on the degree of grafting but also on the graft distribution across PVDF matrix. For instance, at low degrees of grafting, swollen polystyrene grafts are mostly distributed near the surface of the membrane, whilst some parts of its bulk remains ungrafted causing segregation in the polystyrene domains and exerting high resistance to swelling. Consequently, the charge transfer (Li^+) is hindered and the conductivity records low values. As the degree of grafting increases, more swollen polystyrene domains becoming closely distributed throughout the whole matrix causing the ungrafted zone to diminish from the middle of the matrix in a way allowing the swollen polystyrene domains to be interconnected and possibly form a network structure that causes high degrees of swelling in the membranes. This remarkably enhances the charge transfer and allows the conductivity to reach high values (10^{-3} S/cm at room temperature for $Y=50\%$). From these results, it can be stated that the ionic conductivity is determined by three cumulative factors: the swelling of the amorphous phase of the membrane matrix, the filling-up of the formed channels and, importantly, the level of distribution of polystyrene grafts across the membranes. The effect of these three parameters is collective, but the relative contribution depends on the degree of grafting.

The membrane system prepared in this study can be described as a heterogeneous, phase-separated, gel polymer electrolyte membrane. There are at least three phases in the activated membrane: an unswollen crystalline domain, a plasticized and swollen amorphous phase host the major part of the liquid electrolyte and a small volume of electrolyte-filled channels.

4. Conclusions

An alternative polymer electrolyte membrane based on copolymer of PVDF and PS precursor was successfully

prepared by radiation-induced graft copolymerization of styrene onto PVDF films followed by activation with LiPH_6 in EC and DEC. The original structure of PVDF matrix was changed to less crystalline structure with the styrene grafting and the subsequent activation with the liquid electrolyte and such effect was found to be confined to all electrolyte membranes at various degrees of grafting as revealed by DSC analysis. The PVDF-g-PS-based electrolyte membrane has high liquid electrolyte uptake capacity and high ionic conductivity at room temperature, both of which increase with the increase in the degree of grafting. Conductivity of the order of 10^{-3} S/cm was achieved at a degree of grafting of 50%. This is attributed to the high degree of swelling in the amorphous phase of the membrane matrix, the homogenous distribution of polystyrene grafts across the membranes and the confinement of some liquid electrolyte to the small volume of formed channels. Results of the present work suggest that radiation induced-graft copolymerization can be used as alternative method to blending to prepare polymer electrolyte membranes for lithium battery applications.

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