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RESEARCH PAPER

Grafting of Polystyrene and Poly (sodium styrene sulfonate) on the Surface of Poly (vinylidene fluoride) via Atom Transfer Radical Polymerization: Synthesis and Characterization

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ABSTRACT

Atom Transfer Radical Polymerization (ATRP) is a versatile technique for the preparation and design of multifunctional and nanostructured materials for a variety of applications. In this research, we have synthesized novel graft copolymers of poly (vinylidene fluoride)-graft-polystyrene (PVDF-g-PS) and poly (vinylidene fluoride)-graft-poly (sodium styrene sulfonate) (PVDF-*g*-PSSA) via ATRP which have a variety of applications such as the preparation of polymeric membranes. The successful grafting of PS and PSSA on the backbone of PVDF was confirmed using Fourier transform infrared spectroscopy (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H-NMR) analyses. The grafting percentages obtained from ^{1}H-NMR analyses were calculated to be 2%, 13%, and 44% for PVDF-g-PS (I), PVDF-g-PS (II), and PVDF-g-PSSA copolymer samples, respectively. The brush copolymers based on PVDF synthesized in this work can be used for the development of energy storage devices such as lithium-ion batteries.

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1. INTRODUCTION

Since the (first) introduction and development of atom transfer radical polymerization (ATRP) in 1994 by Krzysztof Matyjaszewski et al.[1], this method has attracted attention as a useful method to prepare and synthesize high-tech and engineering polymers and copolymers (such as graft copolymers) [2]. This controlled radical polymerization method faciliates the production of advanced materials with controlled architecture. ATRP enables researchers' control over the topology, composition, and incorporation of predefined functionalities of polymeric materials. Moreover, faciliated synthesis of well-defined gradient, comb copolymers, hyper-branched structured polymers such as stars, inorganic-organic hybrid materials and bioconjugates all become possible [1]. The halogen atoms on the backbone of chemical (macro) initiaitors are generally served as the initiation sites for this polymerization process. ATRP is defined as a well-known catalytic process, and the mediation of ATRP can be done by various redox-active transition metal complexes. Cu^I/L and $X\text{-}Cu^{II}/L$ have been the most frequently used transition metal; however,

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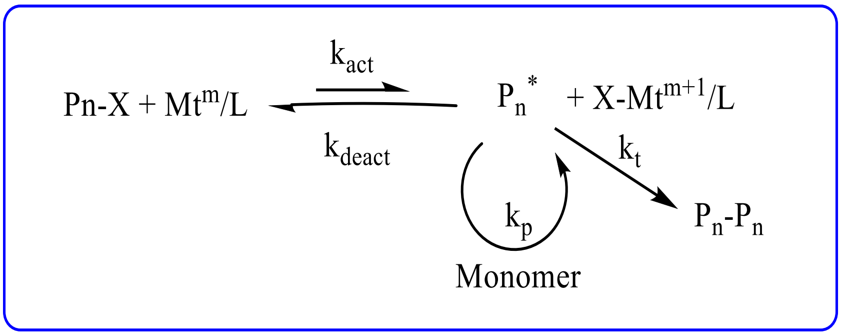
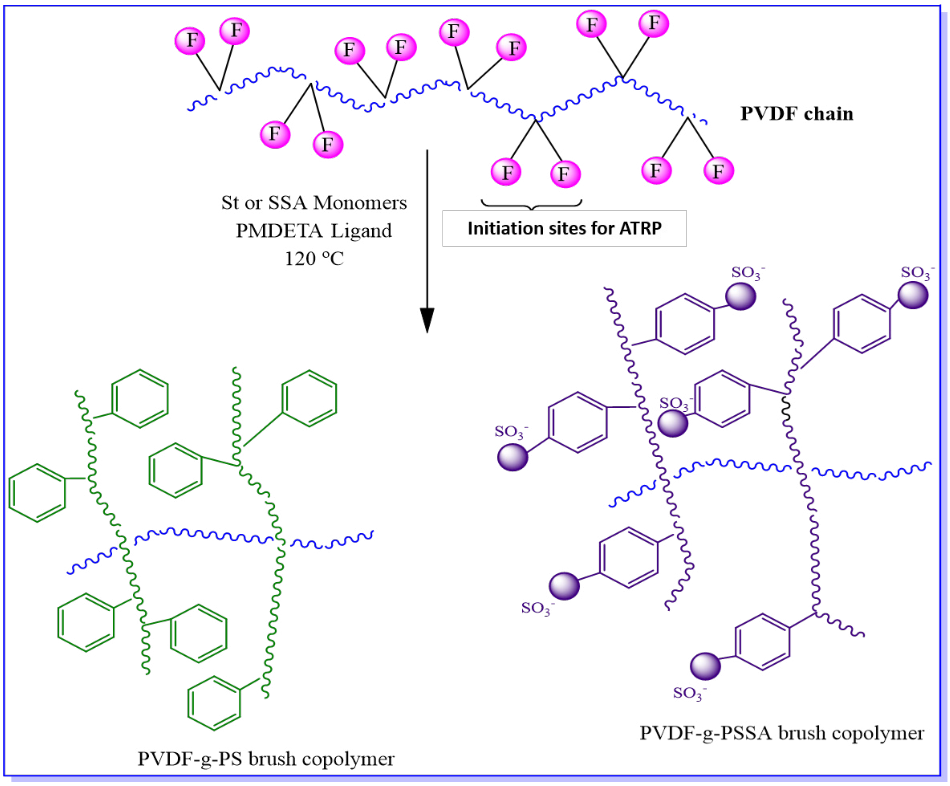
there are some other metals like Ru, Fe, Mo, Os and, etc. which are excellent candidates to be used as the transition metal compounds. The rate of an ATRP reaction depends on the rate of propagation constant and on the concentrations of growing radicals and monomers [3]. The ATRP equilibrium is shown in scheme 1, Where, P_n-X represents the (Macro)initiator used for ATRP polymerization.

A few polymers with high-volume production, such as poly (vinylidene fluoride) (PVDF), poly (vinyl chloride) (PVC), and chlorinated polyolefins, contain repeat units with secondary halogen atoms pendant. Fundamentally, the aforementioned polymers can be engaged as the macroinitiator for preparing different copolymers and functionalized derivatives via ATRP [2]. In other words, the halogen atoms on the backbone of these polymers can play the role of initiation locality for the grafting of other polymers via "grafting from" method and thus design and synthesis of novel brush copolymers (Scheme 2).



Scheme 1. The ATRP Equilibrium [1]



Scheme 2. The role of PVDF as macroinitiator for the synthesis of PVDF-g-PS and PVDF-g-PSSA brush copolymers

In this research, we applied the ATRP method to synthesize PVDF-*g*-PS (types I & II) and PVDF-*g*-PSSA copolymers using PVDF as the macroinitiator. PVDF is a well-known polymeric material for the lithium-ion battery (LIB) application due to its high intrinsic dielectric constant. It has also been used as a binder and polymeric electrolyte [4-6]. The modification of this polymer with the ATRP method and the synthesis of novel polymeric materials based on PVDF can have applications in the development of next-generation LIBs.

2. Research Method

2.1 Materials

Solef® 5120 PVDF (Solvay, Mw= 570000-600000 g/mol) was dried under vacuum at 80 °C for about 24 hours and was used as the macroinitiator. Sodium Styrene sulfonate monomer (SSA monomer, Mn= 206.194 g/mol), N-methyl-2-Pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) as the solvent, styrene monomer (Stabilised) for synthesis (Mn= 104.15 g/mol, Merck), N,N,N',N",N"-pentamethyl diethylenetriamine (PMDETA) for the synthesis (Density= 0.828 g/cm^3 at 20 °C, Mn= 173.30 g/mol) as the ligand of the reaction (ATRP), copper (I) chloride (supplied by Sigma-Aldrich, CuCl) were used for the synthesis of copolymers. Methanol (Extra pure, Dr. Mojallali) was used as a non-solvent in analytical reagent grade for the purification of the final product.

2.2 Synthesis of PVDF-g-PS (I & II) and PVDF-g-PSSA copolymers

The very first step to make the solution ready for ATRP is to create the PVDF solution. To achieve this goal, the dried PVDF was dissolved in NMP (solvent) and stirred for 30 minutes at 80 °C [7]. After the dissolution of PVDF, the styrene monomer was added to the reaction tube. The N_2 gas was purged into the reaction mixture for 20 minutes. PMDETA was used as the ligand in this copolymerization and added in the final step, followed by immersing the reaction mixture inside a silicon oil bath for 48 h at 120 °C. The final product turned into a brownish solution at the end of the reaction.

Extra pure methanol was used as the non-solvent for the purification of products. The final product was dried at 80 °C under vacuum for 24 h. The exact process was used for the synthesis of PVDF-*g*-PSSA copolymer. The SSA monomer was dissolved in DMSO solvent and mixed with the PVDF solution. Table 1 shows the number of ingredients used for the synthesis of copolymers.

Table 1. Molar ratio and weights of the reactants

Samples	[PVDF]	[NMP]	[DMSO]	[St or SSA]	[Monomer]:[PMDETA]:[CuCl]
PVDF-g-PS(I)	0.3 g	2.5 ml	______	0.55 ml	[67.91]:[1.35]:[1]
PVDF-g-PS(II)	0.3 g	2.5 ml	______	0.825 ml	[101.94]:[1.35]:[1]
PVDF-g-PSSA	0.3 g	2.5 ml	2.5 ml	1 g	[68.62]:[1.35]:[1]

2.3 Characterization

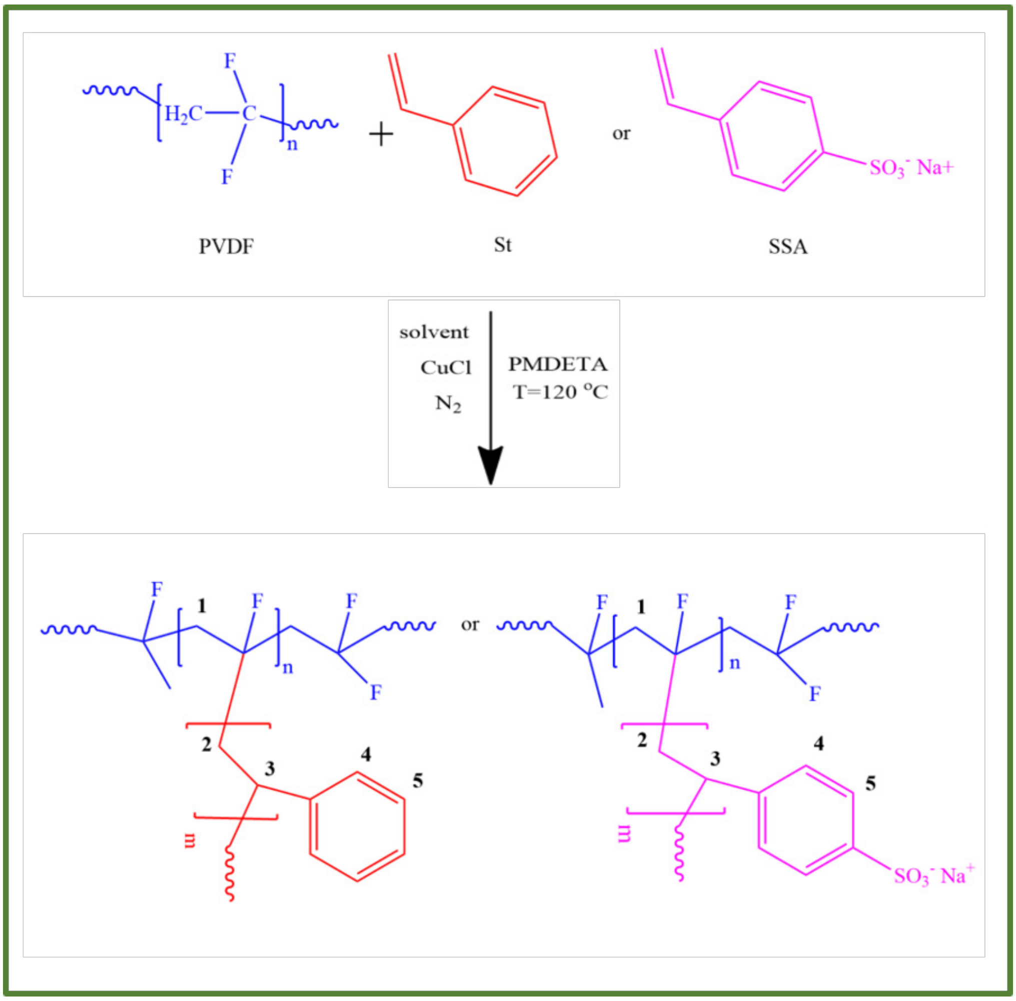
The Fourier transform infrared spectroscopy (FT-IR) spectra of the two extracted copolymer samples PVDF-g-PS(I) and PVDF-g-PSSA were measured with a PerkinElmer Spectrum Version 10.03.06 in the range of 400-4000 cm^{-1}. ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectra of the samples were recorded with a high-quality VARIAN INOVA 500 MHz. All the data obtained from both FT-IR and ^{1}H-NMR analysis were interpreted to prove the accuracy of the graft copolymerization via ATRP, and the calculations related to the grafting percentages were accurately made.

3. Results and Analysis

The illustration below (Fig. 1.) shows the whole process of polymerization of PVDF-g-PS (I & II) and PVDF-g-PSSA.

The PS and PSSA moieties were grafted from the C-F groups of PVDF, according to the mechanism illustrated in Scheme3. Fig. 1 shows the results of FT-IR analyses for pristine PVDF and PVDF-*g*-PS copolymer.

Since the PVDF-*g*-PS (I & II) copolymers both consist of similar molecular structures and functionalities, the FT-IR results were reported for only one of the PVDF-g-PS brush copolymers. As the results show, there is a strong band at 1402 cm^{-1} corresponding to the stretching vibration of C-H bonds, while the bands located at 1275 cm^{-1} and 1178 cm^{-1} are attributed to the vibration of C-F bonds (1178 cm^{-1} and 1275 cm^{-1}, respectively) [8, 9].



Scheme 3. The complete illustration of copolymerization processes applied to synthesize PVDF-g-PS (I & II) and PVDF-g-PSSA via ATRP

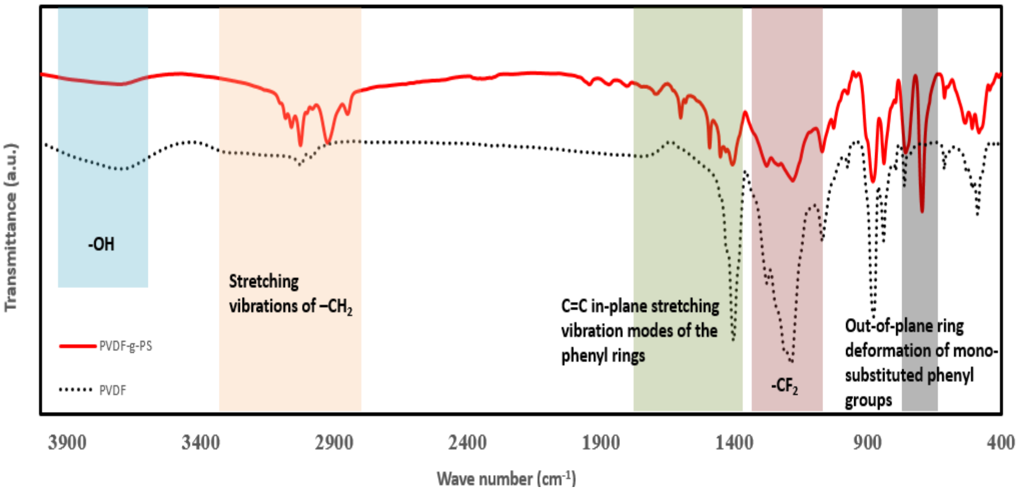


Figure 1. FT-IR spectra of pristine PVDF and PVDF-g-PS copolymer

The peak appeared at 2923.62 cm^{-1} (PVDF-*g*-PS) corresponded to the stretching vibrations of $–CH_2$, C=C in-plane stretching vibration modes of the phenyl rings at 1693.64-1407.54 cm^{-1} and out-of-plane ring deformation of mono-substituted phenyl groups appeared at 697.66 cm^{-1} [10]. These results show that the PS functional groups were successfully grafted on the PVDF.

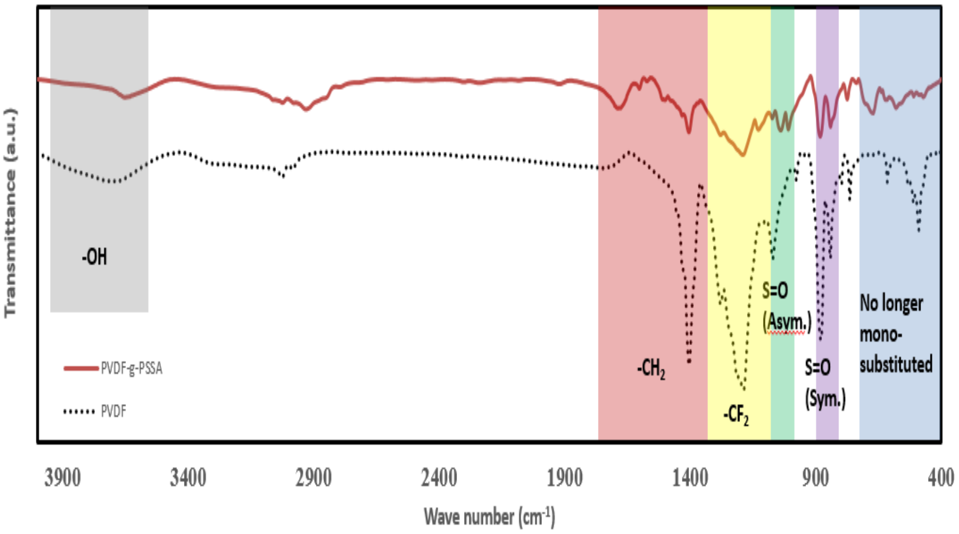
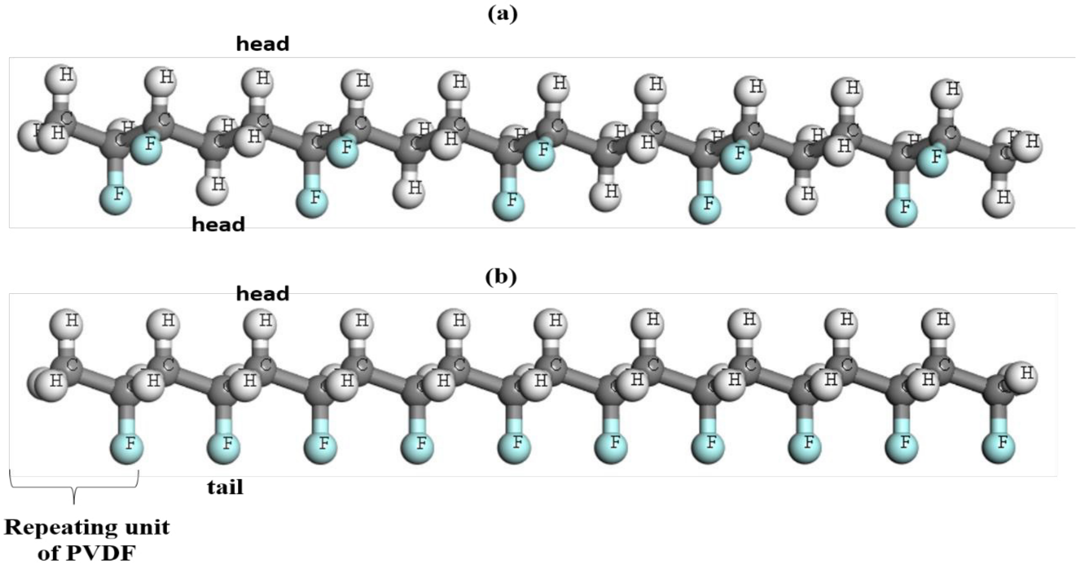


Figure 2. FT-IR spectra of Pristine PVDF and PVDF-g-PSSA copolymer

Fig. 2. shows the FT-IR analysis of PVDF-*g*-PSSA compared to pristine PVDF. The peak occurred at 1039.39 cm^{-1} (PVDF-*g*-PSSA) indicated the asymmetric stretching vibrations of the S=O bond. On the other hand, the peak at 840.26 cm^{-1} corresponded to the symmetric stretching vibrations of the S=O bond [11]. The peaks occurred at the range of 674.49-578.48 cm^{-1} indicated that there was no longer any mono-substituted structure [12].

All the samples were also characterized via ^{1}H-NMR analyses (Figures 3 and 4).



Scheme 4. PVDF chain with (a) head-to-head and (b) head-to-tail conformations

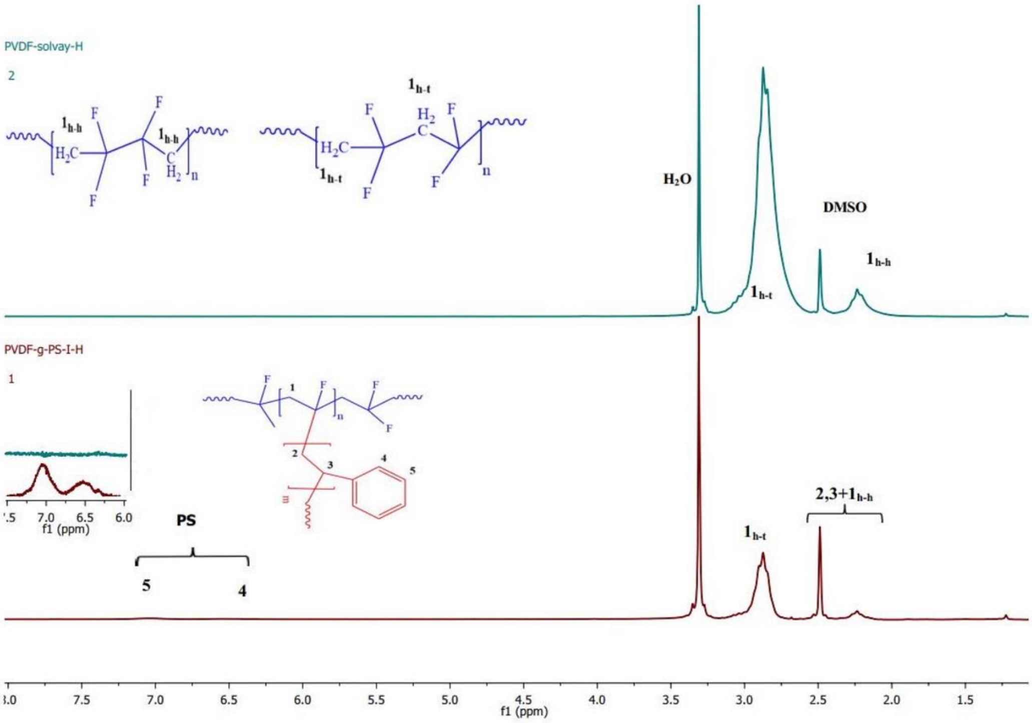


Figure 3. ^{1}H-NMR analysis of pristine PVDF vs. PVDF-g-PS (I)

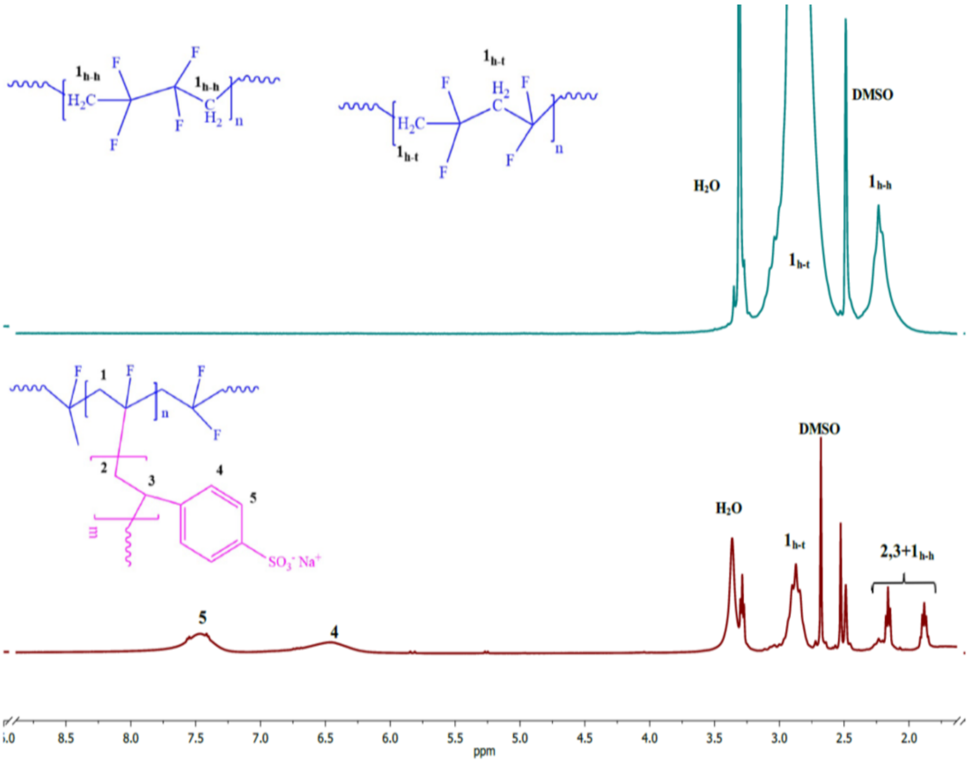


Figure 4. ^{1}H-NMR analysis of pristine PVDF vs. PVDF-g-PSSA

As can be seen, each peak that appeared in the ^{1}H-NMR spectra was assigned to the corresponding protons. The peak visible at 2.3 ppm represented the presence of H_2O in PVDF (Figure 3), and the peak appeared in 2.5 ppm corresponded to the DMSO solvent. The vibrating peaks appeared at the range of 3-3.2 ppm represented the C_6F_{13}-CH_2-CF_2- groups [12-14]. The PVDF used in this research contained head-to-head (h-h) and head-to-tail (h-t) conformations in which their existence was investigated using ^{1}H-NMR analyses (Scheme 4).

The peaks assigned to hydrogen atoms related to the head-to-head and head-to-tail conformations that existed in the PVDF structure appeared in the range of 2.2-2.4 ppm and 2.7-3 ppm, respectively. The percentage of head-to-head and head-to-tail conformations of PVDF was calculated according to the following equations [4, 10, 12]:

$$X_{h-h_{PVDF}}\% = \frac{\frac{I_{h-h}}{2}}{\frac{I_{h-h}}{2}+\frac{I_{h-t}}{2}} \tag{1}$$

$$X_{h-t_{PVDF}}\% = 1 - X_{h-h_{PVDF}}\% \tag{2}$$

According to the Eqs. (1) and (2), the percentage of head-to-head and head-to-tail conformations was calculated to be 8% and 92%, respectively. The peak appeared at the range of 6.25-6.75 ppm for PVDF-*g*-PS sample was assigned to the proton (hydrogen) number 4 of the phenyl ring. The peak appeared at 6.75-7.5 ppm was related to the proton number 5 specified on the chemical structure. The peaks corresponded to the phenyl group in the structure of the copolymer proved that the grafting of the PS on the PVDF had been done successfully.

The grafting percentages of PS and PSSA moieties were calculated to be 2%, 13%, and 44% for PVDF-g-PS (I), PVDF-g-PS (II), and PVDF-g-PSSA copolymers from peak intensity analysis and integration using the equations 3-6, Where X% is the grafting percentage, (I) represents the integration intensity of a specific peak in ^{1}H-NMR, I_{h-h} represents the integration intensity of the peak corresponding the head-to-head conformation of PVDF, I_{h-t} represents the integration intensity of the peak corresponding the head-to-tail conformation of PVDF, respectively. Fig. 4 illustrates the ^{1}H-NMR analysis of pristine PVDF versus the novel PVDF-g-PSSA copolymer. The peak corresponding the solvent (DMSO) appeared at 2.6 ppm, and the peak appearing at 3.5 corresponded to the absorbed water (H_2O) molecule in the structure [15]. The peak at 2.9 ppm was attributed to the head-to-tail (h-t) bonding arrangement of PVDF itself, and the peak detected at 2.3 ppm represented the head-to-head (h-h) conformation of PVDF, respectively [16]. The peak at 1.9 ppm showed the proton vibrations at the positions specified on the structure in the ^{1}H-NMR graph (position numbers 2 and 3). The peaks that appeared at 6.5 and 7.5 ppm were assigned to the proton numbers 4 and 5 specified on the chemical structure. These peaks corresponded to the phenyl group in the structure of the copolymer (aromatic bonding environments in the SSA), proving that the grafting of the PSSA on the surface of PVDF had been done successfully [17].

Calculations for PVDF-g-PS (I & II) and PVDF-g-PSSA copolymers were made by applying the exact numerical value of ^{1}H-NMR peak integration results, which corresponded to the proton number 5 (specified on the structural scheme). Moreover, the integration value of peak corresponding proton number 4 was used in calculations for PVDF-g-PSSA copolymer.

$$X_{PS-or-PSSA}\% = \frac{\frac{I_{4,5}}{1}}{\frac{I_{4,5}}{1}+(\frac{I_{h-h}+I_{h-t}}{2})} \tag{3}$$

For PVDF-g-PS (I) :

$$X_{PS(I)}\% = \frac{\frac{I_5}{1}}{\frac{I_5}{1}+(\frac{I_{h-h}+I_{h-t}}{2})} \tag{4}$$

For PVDF-g-PS (II):

$$X_{PS(II)}\% = \frac{\frac{I_5}{1}}{\frac{I_5}{1}+(\frac{I_{h-h}+I_{h-t}}{2})} \tag{5}$$

And eventually for the PVDF-g-PSSA:

$$X_{PSSA}\% = \frac{\frac{I_4}{1}}{\frac{I_4}{1}+(\frac{I_{h-h}+I_{h-t}}{2})} \tag{6}$$

As the results show, for the same molar values of SSA and St monomers, the grafting percentage of PSSA on the PVDF backbone is higher than the grafting percentage of PS for samples PVDF-g-PSSA and PVDF-g-PS, respectively. This observation can be due to the higher reactivity of SSA in comparsion to St. The reactivity ratios of St (r_1) and SSA (r_2) were reported to be 0.5 and 10 [18], respectively, which are consistent with the results of this study.

4. Conclusion

Brush copolymers based on PVDF were synthesized via ATRP method in this work. According to the characterization results, it was confirmed that PS and PSSA grafted successfully on the surface of PVDF. The grafting percentages were reported as 2%, 13%, and 44% for PVDF-g-PS (I), PVDF-g-PS (II), and PVDF-g-PSSA copolymer samples, respectively. In the same molar values of St and SSA monomers, the grafting percentage of PSSA was higher than PS on the backbone of the PVDF chain, which confirmed the higher tendency of PSSA to be grafted on the backbone of PVDF. Due to the high application of PVDF in the production of energy storage devices, the brush copolymers synthesized in this work have the potential application in this field of technology.

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مقاله تحقیقاتی

پیوند زنی پلی‌استایرن و پلی(سدیم استایرن سولفونات) بر سطح پلی(وینیلیدن فلئوراید) از طریق پلیمریزاسیون رادیکالی انتقال اتم: سنتز و شناسائی

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کلمات کلیدی:

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کوپلیمریزاسیون

پلی(وینیلیدن فلئوراید) (PVDF)

پلی‌استایرن

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چکیده

پلیمریزاسیون رادیکالی انتقال اتم (ATRP) تکنیکی متنوع برای طراحی و تهیه مواد با گروه‌های عاملی مختلف و یا مواد نانوساختار جهت کاربری در بازه گسترده‌ای از کاربردها می‌باشد. در این پژوهش، ما کوپلیمرهای پیوندی نوین پلی(وینیلیدن فلئوراید)-پیوند-پلی‌استایرن (PVDF-g-PS) و پلی(وینیلیدن فلئوراید)-پیوند-پلی (سدیم استایرن سولفونات) (PVDF-g-PSSA) را توسط بهره‌گیری از روش ATRP سنتز نمودیم که کاربردهای فراوانی از جمله در ساخت غشاها دارند. پیوندزنی موفق PS و PSSA بر روی زنجیره اصلی PVDF توسط بهره‌گیری از طیف سنجی مادون قرمز تبدیل فوریه (FT-IR) و نیز آنالیز رزونانس مغناطیسی هسته هیدروژن (1H-NMR) انجام گرفته است. درصد پیوند زنی بدست آمده توسط آنالیز 1H-NMR، مقادیر ۲%، ۱۳% و ۴۴% به ترتیب برای نمونه‌های کوپلیمری پیوندی (I) PVDF-g-PS، (II) PVDF-g-PS و PVDF-g-PSSA محاسبه شد. کوپلیمرهای شانه‌ای بر پایه PVDF که در این کار سنتز شدند می‌توانند برای توسعه وسائل ذخیره‌ساز انرژی مانند باتری‌های لیتیومی مورد استفاده قرار گیرند.

نحوه استناد به این مقاله:

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