



# Article Styrene-Based Copolymer for Polymer Membrane Modifications

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**Abstract:** Poly(vinylidene fluoride) (PVDF) was modified with a styrene-based copolymer. The crystalline behavior, phase, thermal stability, and surface morphology of the modified membranes were analyzed. The membrane surface roughness showed a strong dependence on the styrene-acrylonitrile content and was reduced to 34% for a PVDF/styrene-acrylonitrile blend membrane with a 40/60 ratio. The thermal and crystalline behavior confirmed the blend miscibility of both polymers. It was observed in X-ray diffraction (XRD) experiments that the modified PVDF membranes show a drastic reduction in their crystallinity. The neat PVDF membrane has the highest degradation rate, which decreased with the addition of the styrene-based copolymer.

Keywords: PVDF membrane; membrane modification; crystalline behavior; hydrophilicity

# 1. Introduction

Membrane modification of polymers by blending is a common and easy method that can provide many desirable properties such as solvent resistance, improved processability, hydrophilicity, and high productivity [1]. The poly(vinylidene fluoride) (PVDF) polymer is extensively employed for membrane preparation as it has an exceptional combination of mechanical, chemical, electrical, and thermal properties. However, the hydrophobic property of PVDF causes fouling and decreases the life of the membrane. Various methods for modification of PVDF have been reported [2–5]. In one of these methods, the PVDF membrane surface was modified by grafting with active compounds using high-energy radiation [2]. Another method highlighted PVDF modification using a surface impregnation coating with active compounds such as hydroxypropyl cellulose (HPC) [3]. Radiation treatment was also suggested to create surface defects, which may act as active sites for the attachment of suitable compounds to the surface [4]. It has been well established that the mixing or blending of hydrophobic commercial polymers with active monomers such as acrylic acid increased hydrophilicity and enhanced their properties [5]. A styrene-based copolymer is a commercially available copolymer of styrene and acrylonitrile. Some key properties of styrene-acrylonitrile such as hydrogen bonding are similar to those of polysulfones [6]. A previous report has dealt with sulfonated styrene-acrylonitrile membranes, which were prepared and blended with cellulose acetate for performance enhancement [7]. The miscibility of polyethersulfone (PES) in hydrophilic copolymers containing 1-vinylpyrrolidone and styrene (PVP-S) has also been reported [8]. Ultrafiltration membranes were fabricated from the mixture of PES and (PVP-S) to improve the hydrophilicity of the hydrophobic PES membrane. Grassie and Bain reported the influences of styrene on thermal degradation of polyacrylonitile and influences of acrylonitile on the depolymerization in polystyrence [9]. Cellulose acetate (CA)-styrene-acrylonitrile blend membranes were prepared with an additive like PEG, which achieved a higher flux than a 100% CA membrane [10].

The prepared blend membranes have been effectively used for the aqueous separation of proteins such as BSA, EA, pepsin, and trypsin by ultrafiltration. Styrene-acrylonitrile/PVDF blends were prepared, where a phase separation was observed to occur with time. A transition from homogeneous nucleation and growth to nonlinear spinodal decomposition in the two-phase region was observed by atomic force microscope (AFM) phase imaging [11,12]. In another example, a PVDF/styrene-acrylonitrile blend was prepared by solution blending, where the acrylonitrile segment of the styrene-acrylonitrile copolymer was found to be partially miscible with PVDF [13]. However, the styrene segment reduced the copolymer's polarity and consequently its miscibility with PVDF. Similar results have been reported for styrene-acrylonitrile/PVDF by melt blending [14]. In our earlier study, we reported PVDF/styrene-acrylonitrile blend membranes that exhibited partial miscibility with less than 50 wt. % styrene-acrylonitrile in PVDF for textile wastewater treatment [15]. The prime objective of the present work is to report the crystallinity, phase analysis, thermal stability, and surface morphology of these polymer blends.

## 2. Experimental Section

## 2.1. Materials

Poly(vinylidene fluoride) (PVDF) (Solef<sup>®</sup> 6010) was received from Solvay, India (Mumbai, MS, India), while styrene-acrylonitrile (25% acrylonitrile content) was purchased from Sigma-Aldrich (St. Louis, MO, USA) in pellet form and used as received. N,N-dimethylformamide (DMF) was purchased from Boisar (Thane, MS, India) and used after distillation. Sodium lauryl sulfate (SLS) was purchased from Rankem Fine Chemicals Limited (New Delhi, Inida).

#### 2.2. Preparation of PVDF/Styrene-Acrylonitrile Blend Membrane

The PVDF/styrene-acrylonitrile membranes were prepared with 17.5 wt. % polymer (PVDF and styrene-acrylonitrile with various compositions as described in Table 1) in 82.5 wt. % DMF by a process described in our previous report [16]. The prepared membranes were rinsed with pure water for 10 min and preserved in a 1% formalin solution to prevent drying and microbial growth on the membrane surface. The modification of PVDF with styrene-acrylonitrile is schematically described in Figures 1 and 2.

Membrane	Polym	er Composition (wt. %)	Solvent	Crystallite	Residual	
Wenterune	PVDF	Styrene-Acrylonitrile	ylonitrile (wt. %)		<b>Strain</b> (ε)	
100% PVDF	17.5	-	82.5	174.40	0.08	
10% styrene-acrylonitrile	15.75	1.75	82.5	41.5	0.031	
20% styrene-acrylonitrile	14.0	3.5	82.5	31.1	0.053	
60% styrene-acrylonitrile	7	10.5	82.5	15.6	1.07	
100% styrene-acrylonitrile	-	17.5	82.5	9.6	1.24	





Poly (Styrene acrylonitrile); SAI

Figure 1. Scheme for modification of PVDF.



Figure 2. Schematic diagram of surface modification of the PVDF membrane.

# 2.3. Membrane Characterization

The degree of crystallinity of the various polymer blend membranes were performed on an X-Ray diffractometer (model ULTIMA III) from RICAGU, Tokyo, Japan. XRD patterns provide comprehensive structural information related to the materials. The XRD patterns of the membranes were studied, and their crystallite size and residual strain were analyzed using the Williamson-Hall equation (Equation(1)) [17]. The crystallinity data is given in Table 2.

$$\beta \cos\theta = 4\varepsilon \sin\theta + \frac{K \times \lambda}{t} \tag{1}$$

Here, *K* is a constant valued at 0.9,  $\lambda$  is the wavelength of X-ray radiation used,  $\beta$  is full width at half maximum (FWHM) for the corresponding  $\theta$ , *t* is the crystallite size in angstrom (A°), and  $\varepsilon$  is the generated strain in the structure. The % crystallinity of the membrane was calculated using the Lorentz equation [18]. The X-ray profile was smoothed by a data filtering process using the Savitzky-Golay function, and a baseline was then set up between two theta (2 $\theta$ ) values of 5°–25°. The smoothed profile was deconvoluted into crystalline (sharp peaks) and amorphous (halo regions). Peak information such as position, amplitude, peak area, and FWHM are listed in Table 2.

The crystallinity was calculated as the ratio of the area of crystalline peak to the area of both crystalline and amorphous peaks. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) of the membranes were studied using a thermal analyzer (model SDT 2960) from TA Instruments, New Castle, CA, USA. Approximately 5–15 mg of membrane samples, whose prior thermal history was eliminated, were sealed in aluminum pans, and the thermograms were recorded from ambient to 550 °C at a heating rate of 10 °C/min under a constant 20 mL/min flow of nitrogen gas. The % crystallinity of membranes (*Xc*) was calculated as per the following equation [19].

$$Xc = \frac{\Delta Hf \times 100}{\varphi \times \Delta Hfmt}$$
(2)

 $\Delta Hfm$  is the melting enthalpy for a crystalline PVDF, which is 104.7 J/g as in previous reports [20],  $\Delta Hf$  is the melting enthalpy of the membrane measured by DSC, and  $\varphi$  is the weight fraction of PVDF in PVDF/styrene-acrylonitrile blends. Phase behavior of the polymers and other quantitative studies were performed on a Fourier transform infrared (FTIR) spectrophotometer (model SPECTRUM RX-1) from Perkin-Elmer, Rodgau, Germany, and (model SPECTRUM 100F) from Perkin-Elmer, Waltham, MA, USA, in the attenuated total reflectance (ATR) mode. An atomic force microscope (AFM) (Veeco Instruments, Santa Barbara, CA, USA) was used for imaging topography and F–D curves. AFM images were measured in the tapping mode (air) with 20–80 N/m using a gold-coated (GC) silicon-nitride tip with a spring constant between 0.01 and 0.10 N/m and frequency between 85 and 155 KHz.

			Lorentz	Function				Gauss F	Function	
Membranes	Crystalline Area Amorpho			ohous Area Crystalline Area				Amorphous Area		
	Area	FWHM	Area	FWHM	Crystallinity (%)	Area	FWHM	Area	FWHM	Crystallinity (%)
100% PVDF	273.2	0.37	814.6	2.60	25.11	225.5	0.47	706.4	2.54	24.20
10% styrene-acrylonitrile	137.5	0.25	616.9	1.83	18.25	203.7	0.54	965.6	4.01	17.42
20% styrene-acrylonitrile	224.9	0.62	1130.6	3.87	16.59	176.7	0.73	1070.6	4.71	14.17
60% styrene-acrylonitrile	102.7	0.42	657.1	3.75	13.51	69.6	0.54	653.9	4.23	9.62
100% styrene-acrylonitrile	64.6	0.99	1305.2	7.73	4.72	44.3	0.8	819.9	7.31	5.13

**Table 2.** Crystalline and amorphous analysis of PVDF/styrene-acrylonitrile membranes by the Lorentz function and Gauss function.

## 3. Results and Discussion

# 3.1. Study of Crystal Size and Crystallinity of Blend Membranes

The XRD patterns of modified PVDF are shown in Figure 3. Figure 3a shows the pattern for 100% PVDF membrane, which has the largest crystallite size of 174.4 A°. It shows three significant peaks at 2 $\theta$  angles of 18.59°, 20.12°, and 26.61° with intensities of 738.42, 552.76, and 242.90, respectively. These correspond to the Miller indices of (0, 2, 0), (1, 1, 0), and (0, 2, 1), respectively [21]. Two of these indices—(0, 2, 0) and (0, 2, 1)—correspond to an  $\alpha$ -phase structure while (1, 1, 0) is a  $\beta$ -phase structure [22]. A comparison of the data for the 100% PVDF membrane with styrene-acrylonitrile blend membranes shows two prominent  $2\theta$  peaks at  $18.59^{\circ}$  and  $20.12^{\circ}$ . The intensities of the three diffraction peaks at 18.59°, 20.06°, and 26.61° vary progressively for the 10%, 20%, and 60% styrene-acrylonitrile blends membranes, while the amorphous halo becomes more pronounced as can be seen in Figure 3. In the 10% styrene-acrylonitrile and 60% styrene-acrylonitrile blend membranes, the  $18.59^\circ$  peak intensity reduces progressively to 716 and finally to 288 from a value of 759 for 100%PVDF (Figure 3a–d). This indicates the emergence of strain in the polymer crystallites with the blending of a second polymer and is given in Table 1. The peak intensities also increase at the Miller indices (1, 1, 0) for the styrene-acrylonitrile blend membranes. It reflects the increase in  $\beta$  phase structure for these blend membranes. The peak at  $26.61^{\circ}$  is the most affected and almost disappeared in the 60% styrene-acrylonitrile blend membrane. Strong crystalline peaks of PVDF (Figure 3a), were replaced by weaker peaks in the XRD patterns of blend membranes as shown in Figure 3b-d. This also confirms the blending of styrene-acrylonitrile in PVDF and signifies the decrease in crystallite size and increase in residual strain in the structure of the blend membranes with an increase in styrene-acrylonitrile content [23]. The XRD pattern of styrene-acrylonitrile (Figure 3e) shows two amorphous halos at  $2\theta$ angles of  $13.54^{\circ}$  and  $19.6^{\circ}$  with intensities 289 and 188, respectively. These halo sections have the Miller indices of (0) and (3, 2, 1), respectively. These XRD results are in order for phenyl acrylonitrile. Crystallinity of 100% PVDF membranes is the highest at 25.11% and decreases with an increase in styrene-acrylonitrile content. The crystallinity analyzed with the Lorentz approach for 10% and 60% styrene-acrylonitrile blend membranes reduces to 18.25% and 13.51%, respectively, and is given in Table 2. Crystallinity data achieved from both the Lorentz and Gauss approaches also indicate the increase in amorphous character of membranes with styrene-acrylonitrile content.



Figure 3. X-ray diffraction of styrene-acrylonitrile-blended PVDF membranes.

# 3.2. Study of Thermal Behavior of Blend Membranes

Figure 4 shows the DSC thermograms for 100% PVDF, 10% styrene-acrylonitrile, 60% styrene-acrylonitrile blends, and 100% styrene-acrylonitrile membranes. PVDF has a glass transition temperature range of -40 to -25 °C [20]. The melting point (Tm) increased from 171.4 °C for the 100% PVDF membrane to 172.5 for the 10% styrene-acrylonitrile blend membrane as shown in Table 3. However, it then decreased to 169 °C. The 100% styrene-acrylonitrile has the melting point of 220 °C [24], which is 28% higher than the melting point of 100% PVDF. The loss of crystalline nature in PVDF membranes modified with higher styrene-acrylonitrile blend membrane decreases to 169 °C. It possesses a high melting point of the 60% styrene-acrylonitrile blend membrane decreases to 169 °C. It possesses a high melting point and good thermal properties due to the presence of the phenyl ring in the structure [24]. All membranes exhibited a marginal weight loss in a 50 to 200 °C temperature range, which is attributed to the evaporation of moisture and residual solvents present in the sample. The 100% PVDF membrane showed the minimum weight loss and the highest degradation temperature (Td). It starts to degrade at 417.5 °C and degradation becomes significant at 477.5 °C as shown in Figure 5a.



**Figure 4.** Melting behavior of styrene-acrylonitrile-blended PVDF membranes. (a) 100% PVDF; (b) 10% styrene-acrylonitrile blend; (c) 60% styrene-acrylonitrile blend; (d) 100% styrene-acrylonitrile membranes.



**Figure 5.** (a) Degradation behavior; (b) Degradation rate of styrene-acrylonitrile-blended PVDF membranes.

Membrane	Melting Pt. (Tm), $^{\circ}$ C	∆ <i>Hf,</i> J/g	<b>PVDF</b> Content	$\Delta H f$ , PVDF, J/g
100% PVDF	171.40	60.77	1.00	60.77
10% styrene-acrylonitrile	172.5	37.60	0.90	41.77
60% styrene-acrylonitrile	169	10.93	0.40	27.31

**Table 3.** Melting point (Tm), melting enthalpy ( $\Delta H f$ ) of membranes obtained from a differential scanning calorimeter (DSC).

Similarly, the degradation of the 10% styrene-acrylonitrile blend membrane starts at 368  $^{\circ}$ C as mentioned in Table 4. They also exhibit a lower degradation temperature than the 100% PVDF membrane. The decrease in degradation temperature of the blend PVDF membrane was observed with an increase in its styrene-acrylonitrile content. The 100% styrene-acrylonitrile membrane starts degrading at 340 °C and degrades almost 92% at 430 °C. Its degradation curve, presented in Figure 5b, shows two peaks, which may be due to the presence of two polymers in the structure: polystyrene and polyacrylonitrile. The first peak corresponds to the acrylonitrile content of the styrene-acrylonitrile polymer, which is present in a lesser proportion and degrades at a lower temperature. However, it has a higher melting temperature than styrene; hence, styrene-acrylonitrile has a higher Tm than the pure polystyrene polymer. This decrease in degradation temperature of blend PVDF polymer is the result of different bond energies for the C–F, C $\equiv$ N, and C-phenyl bonds present in the blends. The bond energy of a C–F bond is 20% higher than that of a C-phenyl bond, while the bond energy of a C $\equiv$ N bond is even lower than a C-phenyl bond. The 100% PVDF membrane has the highest degradation rate, which reduces with increasing styrene-acrylonitrile content of the blend membranes. The styrene-acrylonitrile blend PVDF polymer membranes displayed two degradation temperature peaks, which were clearly observed for the 60% styrene-acrylonitrile blend membrane. However, thermodynamically compatible responses were observed in the thermograms of the blend membranes and only one Tm was observed. Analysis of DSC and TGA also confirmed the appropriate styrene-acrylonitrile blending with the PVDF polymer in blend membranes.

Membrane	Td (Start) °C	Res. wt. % (Start)	Td (Peak) °C	Td (Final) °C	Res. wt. % (Finish)	∆Td	$\Delta$ Res wt. %
100% PVDF	417.5	97.5	477.5	495	30.4	77.5	67.1
10% styrene-acrylonitrile	368	97.2	467	493	36.4	125	60.8
20% styrene-acrylonitrile	355	97	460	491.5	38	136.5	59.0
60% styrene-acrylonitrile	350	96.1	469	480	18.5	130	77.6
100% styrene-acrylonitrile	340	95.5	405	430	3.5	90	92.0

Table 4. Degradation temperatures of PVDF blend membranes.

# 3.3. FTIR-ATR Analysis of Blend Membranes

PVDF is known to exhibit polymorphism. Gregorio and Borges reported [24] that it may be present in four different well-known crystalline structures; the orthorhombic  $\alpha$ ,  $\beta$ , and  $\delta$  phases, and the monoclinic  $\gamma$  phase. The FTIR-ATR fingerprint regions of the top surface of 100% PVDF, 100% styrene-acrylonitrile membranes, and the blend membranes are shown in Figure 6a. In the case of the 100% PVDF membrane, the peaks at 762 cm<sup>-1</sup> (skeletal bending), 615 cm<sup>-1</sup> (CF<sub>2</sub> bending), and 798 cm<sup>-1</sup> (-CH<sub>2</sub> rocking) represent the typical α-phase with 511 cm<sup>-1</sup> (CF<sub>2</sub> bending) and 840 cm<sup>-1</sup> (-CH<sub>2</sub> rocking) as typical β-phase peaks. The peaks at 1178 cm<sup>-1</sup> and 1275 cm<sup>-1</sup> show the in-plane stretching of C–F bonds [25]. According to Bottino *et al.* [26], this signifies the change in composition of that particular phase. The α-phase, trans di-substituted alkene peak of 975 cm<sup>-1</sup> and 798 cm<sup>-1</sup> for the 100% PVDF membranes are significantly reduced in the styrene-acrylonitrile blend membranes. The presence of acrylonitrile (-CN) group in the blend membranes was confirmed by the presence of a minor peak at 2237 cm<sup>-1</sup>. The peaks at 760 cm<sup>-1</sup> and 513 cm<sup>-1</sup> are the shifted peaks previously observed at 762 cm<sup>-1</sup> and 511 cm<sup>-1</sup>, respectively, which represent the peaks of the

 $\alpha$ -phase and the  $\beta$ -phase of (-CH<sub>2</sub> rocking) the 100% styrene-acrylonitrile. The peak at 700 cm<sup>-1</sup> represents a mono-substituted benzene, which is the characteristic peak of styrene present in the styrene-acrylonitrile blend membranes. However, the bending vibration band of the benzene ring plane had split into two independent peaks at respectively 760 and 790 cm<sup>-1</sup> for 60% styrene-acrylonitrile and 10% styrene-acrylonitrile membranes.



**Figure 6.** Fourier transform infrared (FTIR)-attenuated total reflectance (ATR) spectra of (a) styrene-acrylonitrile; (b) SAN: styrene-acrylonitrile blended PVDF membranes.

#### 3.4. Phase Analysis of Membranes

FTIR-ATR spectra of membranes given in Figure 6b indicate the significant presence of  $\alpha$  and  $\beta$  phases in their structure. The  $\alpha$  and  $\beta$  phases of PVDF has been investigated for phase inversion membranes [27,28]. The  $\beta/\alpha$  phase ratio in the surface layer can be estimated by comparing the absorbance of typical  $\beta$  and  $\alpha$  peaks at 840 cm<sup>-1</sup> and 762 cm<sup>-1</sup>, respectively. The calculated  $\beta/\alpha$ phase ratio for 100% PVDF, 10% styrene-acrylonitrile blend, 20% styrene-acrylonitrile blend, 60% styrene-acrylonitrile blend, and 100% styrene-acrylonitrile membranes are 1.33, 1.57, 1.60, 1.67, and 0.3026, respectively, and presented in Figure 6.  $A_{\beta}^{508}$  was considered as the absorbance for the  $\beta$ -phase of 100% styrene-acrylonitrile membranes instead of  $A_{\beta}^{508}$ . An increase in the  $\beta/\alpha$  phase ratio with an increase in the styrene-acrylonitrile content of the blend membranes was observed. The mobility of PVDF decreased in the presence of styrene-acrylonitrile polymer chains in the system, which might cause a higher degree of chain entanglement. An index  $A\beta$  was used to detect the crystal forms of PVDF with solution-blended styrene-acrylonitrile. The styrene-acrylonitrile is a highly amorphous polymer with a less oriented structure and high chain mobility. It was obvious that the content of the  $\beta$ -phase of PVDF has a tendency to decrease with the increment of styrene-acrylonitrile (10% and 60%). However, the degree of crystallinity of PVDF decreased with the increasing content of presence of amorphous styrene-acrylonitrile. Styrene-acrylonitrile is a copolymer of styrene and acrylonitrile comonomer. The nonpolar styrene segment in the styrene-acrylonitrile copolymer further reduces the homogenous and partially miscible zones. In the addition of styrene-acrylonitrile to PVDF, there may be good miscibility with PVDF such that nonpolar styrene around acrylonitrile comonomer has a greater effect on the crystallization of PVDF.

# 3.5. Surface Investigation of Styrene-Acrylonitrile-Modified PVDF Membranes

The surface textual properties of membranes can have serious implications on membrane performance and fouling. Thus, the quantitative understanding of nanometer- to micrometer-scale surface morphology was carried out using AFM. AFM images were obtained over two different areas:

an area of 5  $\mu$ m × 5  $\mu$ m and a small area of 1  $\mu$ m × 1  $\mu$ m. The large size was imaged to investigate the surface morphology of the membranes, while the small size images were used to determine the pore size and its distribution. The AFM images are given in Figure 7. Roughness is one of the most important surface properties as it has a strong influence on adhesion (fouling). The membrane with relatively high roughness is prone to increased fouling on its surface because roughness increases surface area, which in turn increases the number of contact points between the foulants and the surface. Surface roughness also affects other parameters that can influence the fouling rate [29]. The rough surfaces also have a reduced repulsive energy barrier compared to smooth surfaces, indicating that particle deposition is more likely on the former.



**Figure 7.** Atomic force microscope (AFM) of top surface of styrene-acrylonitrile-blended PVDF membranes. (a) 100% PVDF; (b) 60% styrene-acrylonitrile blend; (c) 100% styrene-acrylonitrile membranes.

Table 5 and Figure 8 contain the parameters related to the average surface roughness, mean height, and peak-valley ratio for all investigated PVDF and styrene-acrylonitrile blend membranes. The 100% PVDF membrane possesses the maximum average roughness and root mean square (RMS) roughness among the investigated membranes. The membrane surface roughness was reduced with styrene-acrylonitrile blending. The average roughness was reduced by 34% in 60% styrene-acrylonitrile blend membranes compared to 100% PVDF membranes. The reduced roughness led to an improvement in the anti-fouling characteristics of the membrane; reduced fouling was observed in the 60% styrene-acrylonitrile blend membranes. The 100% styrene-acrylonitrile membrane has the least average and RMS roughness and therefore exhibited excellent anti-fouling characteristics. Our AFM observations and inferences for the styrene-acrylonitrile blend membranes correspond well with our observations from permeability and hydrophilicity analysis.

Table 5. Surface characteristics of styrene-acrylonitrile-modified PVDF membranes.

Membrane	Average Roughness (nm)	Roughness RMS (nm)	Mean Height (nm)	Peak-Valley Difference (nm)
100% PVDF	17.5	59.1	64.4	143
60% styrene-acrylonitrile	11.5	34.5	51.42	218
100% styrene-acrylonitrile	7.8	30.05	29.67	251



**Figure 8.** AFM line profile of the top surface of styrene-acrylonitrile-blended PVDF membranes. (a) 100% PVDF; (b) 60% styrene-acrylonitrile blend; (c) 100% styrene-acrylonitrile membranes.

# 4. Conclusions

PVDF/styrene-acrylonitrile blend membranes were successfully prepared by phase inversion in the presence of DMF. PVDF/styrene-acrylonitrile blends behave as miscible blend systems, which exhibit good polymer-polymer interactions below 40% compositions. The crystalline nature of the blends clearly depended on their styrene-acrylonitrile content. The addition of styrene-acrylonitrile to PVDF enhanced the  $T_m$  value of the modified PVDF. However, the  $T_m$  value reduced in PVDF blends with concentrations of styrene-acrylonitrile greater than 40%. Our thermal stability results confirm good miscibility of PVDF/styrene-acrylonitrile. The absorbance for the  $\beta$ -phase of styrene-acrylonitrile appeared in all blend compositions. Further, FTIR-ATR results indicate that the PVDF/styrene-acrylonitrile blends were completely mixed on a molecular scale. AFM investigations also revealed the decrease in average surface roughness and the improvement in anti-fouling ability of styrene-acrylonitrile-modified membranes with an increase in their styrene-acrylonitrile content.

**Author Contributions:** H.S. conceived, designed, and performed the experiments and analyzed the data; H.L. and D.P. contributed for materials/analysis tools; G.A. and J.H.K. supervised the work; H.S. and H.L. wrote the paper.

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