

# Grafting Poly(Vinyl Amine-co-Acrylic Acid)s on Poly(Vinylidene Fluoride) Membranes

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## SYNOPSIS

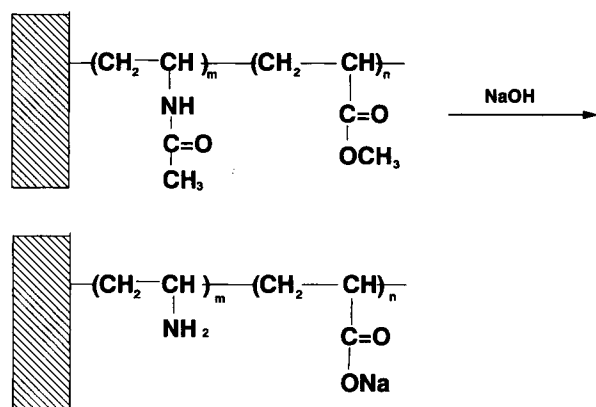
In this study, *N*-vinylacetamide (NVA) was graft-polymerized and graft-copolymerized with acrylamide (AAm) onto plasma-activated surfaces. The polymer compositions of the grafted layer were estimated from X-ray photoelectron spectroscopy spectra. *N*-vinylacetamide was enriched in the grafted polymers in all regions of the monomer compositions. The primary amine groups could be densely introduced on the surface by hydrolyzing the grafted poly(vinylacetamide-co-acrylamide). © 1994 John Wiley & Sons, Inc.

In the series of Ikada and co-workers' studies,<sup>1-3</sup> various monomers were graft-polymerized on polymer surfaces. Their method is useful to densely introduce functional groups on the surface. However, a polymer carrying a primary amine in the side chain has not yet been grafted. The primary amine group can react with various functional groups, such as carboxylic acids, aldehydes, and isocyanates, and form a covalent bond. Thus it can be used to immobilize enzymes, antibodies, and synthetic polymers on the polymer surface. Cells with negatively charged surfaces effectively adhere onto a positively charged surface. In tissue culture, a surface carrying amine groups is useful when weakly adherent cells are cultured. In this study, *N*-vinylacetamide (NVA) was graft-polymerized and graft-copolymerized with acrylamide (AAm) onto the plasma-activated surfaces. The amine groups were generated by hydrolyzing grafted NVA residues of the graft polymer.

The membrane substrate used was a porous poly(vinylidene fluoride) (PVdF) membrane (Cat. No. GVHP02500, Millipore Co., Bedford, MA) with a pore size of 0.22  $\mu$ m. Electrophoretic grade AAm was obtained from Wako Pure Chemical (Osaka, Japan). *N*-vinylacetamide was kindly donated by Dr. Marumo (Showa Denko, Ltd., Oita, Japan). These materials were used as obtained. The PVdF membranes were treated by an Ar plasma using a

glow discharge reactor, Model LCVD-19, manufactured by Shimadzu Corp. (Kyoto, Japan). The pressure in the reactor was kept at 0.1 torr by introduction of Ar gas. After that, a plasma was generated at 30 W, and the membranes were treated with the plasma for 10 s. After plasma treatment, the membrane were exposed to air for ca. 1 h. The radicals on the surface reacted with oxygen and were transformed to peroxide groups. Subsequently, the membranes were immersed in 10 wt % aqueous mixtures of monomers in glass ampoules. After vigorous degassing, the ampoules were sealed and kept at 60°C for 25 or 60 min to allow graft polymerization to proceed. The nongrafted polymer was removed from the grafted films by extraction with water. The grafted films were immersed in 2N NaOH at 60°C for 2 h to hydrolyze the side chains ( $-\text{NHCOCH}_3$ ) of *N*-vinylacetamide to ( $-\text{NH}_2$ ), and the side chains ( $-\text{CONH}_2$ ) of acrylamide to ( $-\text{COONa}$ ) (Fig. 1). The membrane surfaces were analyzed before and after hydrolysis with an X-ray photoelectron spectrometer (XPS) (Shimadzu, Kyoto, Japan) with a MgK $\alpha$  X-ray source (1254 eV at 8 kV; 30 mA).

The grafted surfaces were analyzed by measuring core-level spectra of C<sub>1s</sub>, O<sub>1s</sub>, N<sub>1s</sub>, and F<sub>1s</sub> with XPS. The XPS spectra of the nontreated PVdF membrane were composed of a high-intensity F<sub>1s</sub> peak and doublet C<sub>1s</sub> peaks. Upon grafting, it is anticipated that the F<sub>1s</sub> peak intensity decreases, and O<sub>1s</sub> and N<sub>1s</sub> peaks derived from poly(NVA-co-AAm)s ap-



**Figure 1** Hydrolysis of grafted poly(vinylacetamide-co-acrylamide).

pear. The graft polymerization was carried out in aqueous mixtures of NVA and AAm. At a grafting time of 25 min,  $O_{1s}$  and  $N_{1s}$  peaks appeared, but the  $F_{1s}$  signals from the base PVdF membrane were still observed. When the graft polymerization proceeded for 60 min, the  $F_{1s}$  signals almost disappeared. The sampling depth of the photoemitted electrons at a  $90^\circ$  takeoff angle is typically ca. 50 Å.<sup>4</sup> The photoemitted electrons from the F atoms, which were located more than 50 Å underneath the surface, could not emerge from the surface. The surfaces were covered by grafted layers thicker than 50 Å. In order to graft a NVA homopolymer, the graft polymerization was carried out in a NVA solution. However, it did not effectively proceed. The  $O_{1s}$  and  $N_{1s}$  peaks appeared, but a strong  $F_{1s}$  signal was still observed even after 60 min grafting time. Stackmann et al.<sup>5</sup>

and Akashi et al.<sup>6</sup> reported that peroxides could not effectively initiate polymerization of NVA. In our graft polymerization, the peroxide groups on the surface were utilized to initiate graft polymerization. This may be the cause of the poor efficiency of graft polymerization of NVA.

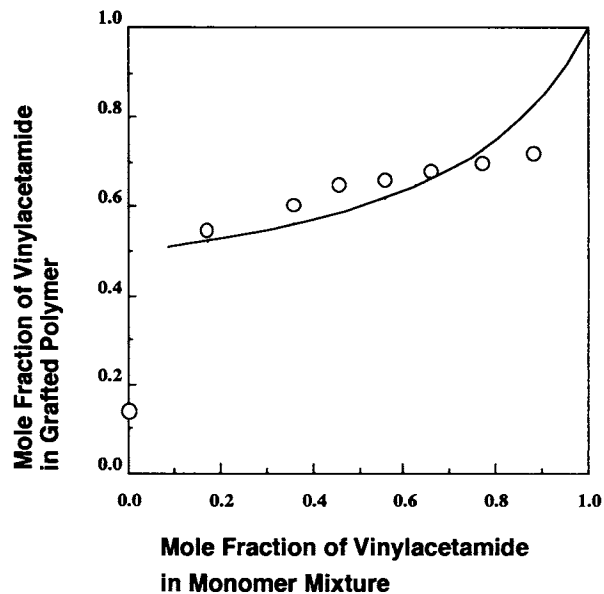
The polymer compositions of the grafted layer were estimated from the XPS analysis. The atomic compositions of the grafted surfaces before and after hydrolysis were evaluated from the intensity of XPS spectra using factors 1, 2.9, 1.5, and 4.3 for C, O, N, and F, respectively<sup>7</sup> (see Table I). The stoichiometrical atomic ratio of poly(acrylamide) (PAAm) grafted surface is C : O : N : F = 1.0 : 0.251 : 0.268 : 0.016. The theoretical atomic ratio for the surface thoroughly covered by PAAm is C : O : N : F = 1.0 : 0.33 : 0.33 : 0.0. The low amount of F atoms on the grafted surfaces indicates that the surface was mostly covered by PAAm. The ratio of O : N was well coincided with the theoretical value. However, the amounts of O and N atoms were lower than the expected values. These comparatively low values probably resulted from surface contamination by hydrocarbon (from pump oil contamination).

The atomic ratios of N/O of the grafted surfaces should be 1 in spite of the compositions of the grafted copolymers because both AAm and NVA monomer units carry one oxygen and one nitrogen atom. When the grafted copolymers are hydrolyzed, AAm and NVA units in the grafted copolymers are converted to acrylic acid (AA) and vinyl amine (VA), respectively (Fig. 1). The acrylic acid residue has two oxygen atoms but no nitrogen atoms. On the other

**Table I** Relative Atomic Ratios of Surfaces of Grafted Membranes as Determined by XPS

Mole Fraction of Vinylacetamide in Monomer Mixture	Graft Polymerization Time (min)	Grafted Membranes			Hydrolyzed Grafted Membranes		
		O/C	N/C	F/C	O/C	N/C	F/C
0.0	60	0.251	0.268	0.016	0.432	0.033	0.032
0.085	25	0.163	0.141	0.490 <sup>a</sup>	0.177	0.091	0.454 <sup>a</sup>
0.173	60	0.254	0.308	0.045	0.303	0.182	0.051
0.264	25	0.197	0.205	0.312 <sup>a</sup>	0.272	0.191	0.186 <sup>a</sup>
0.358	60	0.248	0.307	0.073	0.279	0.220	0.048
0.455	25	0.235	0.290	0.096	0.264	0.241	0.089
0.556	60	0.245	0.282	0.048	0.266	0.257	0.060
0.661	25	0.233	0.250	0.067	0.259	0.270	0.072
0.770	60	0.222	0.291	0.085	0.234	0.279	0.060
0.882	25	0.220	0.253	0.109	0.238	0.310	0.091
1.0	60	0.200	0.185	0.311 <sup>a</sup>	0.183	0.096	0.376 <sup>a</sup>
Plasma-treated membrane	Without grafting	0.095	0.019	0.882	—	—	—

<sup>a</sup> These comparatively high values indicate the insufficient amounts of the graft polymer.



**Figure 2** Polymer composition plotted against the monomer composition for graft copolymerization of *N*-vinylacetamide and acrylamide on plasma activated surfaces. (O); determined using X-ray photoelectron spectrometer, (—); calculated by kinetic theory of copolymerization using  $r_1 = 0.5$  and  $r_2 = 0$ .

hand, the VA residue has one nitrogen atom but no oxygen atoms. The N/O atomic ratios reflect the compositions of the grafted polymers. The molar ratios of VA in grafted copolymers can be expressed using the N/O atomic ratios as

$$\frac{[\text{VA}]}{[\text{AA}] + [\text{VA}]} = \frac{2\text{N/O}}{1 + 2\text{N/O}} \quad (1)$$

[VA] and [AA] are molar concentrations of VA and AA in the hydrolyzed graft polymer. The polymer compositions,  $[\text{NVA}]/\{[\text{AAm}] + [\text{NVA}]\} = [\text{VA}]/\{[\text{AA}] + [\text{VA}]\}$ , which were evaluated using Eq. (1), were plotted against the monomer compositions in the monomer mixtures in Figure 2. *N*-vinylace-

tamide was enriched in the grafted polymers in all regions of the monomer compositions. Monomer reactivity ratios  $r_1$  and  $r_2$  were estimated as 0.5 and 0 using a Fineman-Ross plot. The polymer composition curve calculated using  $r_1$  and  $r_2$  is also shown in Figure 2. The AAm radical prefers to add the NVA monomer. This resulted in enrichment of NVA in the graft polymers.

Although the efficiency of grafting polyNVA is not high, the copolymers of high NVA content can be easily grafted on the surface by copolymerization of NVA with AAm. The primary amine groups could be densely introduced on the surface by hydrolyzing the grafted poly(NVA-co-AAm). After hydrolysis, the grafted chains carry not only primary amine groups but also carboxyl groups. *N*-vinylacetamide can be copolymerized with vinyl acetate and methyl methacrylate.<sup>6</sup> Carboxyl groups are not desirable in the grafted chains; NVA should be copolymerized with these monomers. Vinyl acetate in the copolymers is hydrolyzed to nonionic vinyl alcohol. Methyl methacrylate is hardly hydrolyzed.

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