Radiation-Initiated Graft Copolymerization of 4-Vinylpyridine onto Polyethylene and Polytetrafluoroethylene Films and Anion-Exchange Membranes Therefrom

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ABSTRACT: Radiation-initiated graft copolymerization of 4-vinylpyridine (4VP) onto low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) films was carried out by γ-rays from ^{60}Co source in nitrogen atmosphere. The direct method of multiple grafting was used, connected with posteffect taking place at irradiation doses from 1 to 35 kGy. Thus the monomer diffused into the polymer matrix together with the stepwise generation of free radicals to reduce the thickness of the nongrafted layer. The grafting proceeds in the amorphous phase of the polymers which is further amorphized by the irradiation. Copolymers with grafting degree (P) from 17 to 75% for LDPE and from 0.7 to 13% for PTFE were obtained. The dependence of the degree of grafting of 4VP on irradiation dose was established. The spectral and thermodynamic properties of the synthesized copolymers were studied. The degree of crystallinity was found to decrease and a two-stage mechanism of thermooxidative destruction was observed. The synthesized copolymers contain pyridine groups determining their anion-exchange properties. The initial pyridine groups in the grafted copolymers were quaternized. Some of the basic characteristics, such as water content and specific electric resistance of anion-exchange membranes (AEM) were studied depending on the grafting degree of 4VP. The ionomers studied possess high transport number ($\bar{t}_- \sim 0.8$–0.9), good diffusion characteristics (9.2×10^{-8}–1.7×10^{-7} cm^2/s), and suitable tensile properties. The AEM obtained, combined with the cation exchange membranes we have synthesized earlier on the same polymeric basis, can be used successfully in various electrodialysis processes. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1469–1475, 1997

Key words: radiation grafting; 4-vinylpyridine; polyethylene; polytetrafluoroethylene; membranes; properties

INTRODUCTION

Radiation-induced grafting is a well-known method for introduction of functional groups into different polymer matrices by specially selected monomers. A number of papers were published on radiation graft copolymerization of polar nitrogen-containing monomers onto polymer films to obtain ionomers for versatile applications.[1–6] They are used as anion-exchange membranes in electrodialysis processes, water desalination,[7] carriers for immobilization of medical products,[8] separators in alkaline batteries,[9] etc.

The grafting of 4-vinylpiridine (4VP) onto low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) films by irradiation from ^{60}Co γ-source or high energy electron beam (from an accelerator) is a promising method for prepara-

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tion of anion-exchange membranes (AEM) combining the valuable properties of the initial polymers (mechanical strength, thermal and chemical resistance) with the ion-exchange properties of the grafted poly-4VP (P4VP). Kabanov and colleagues[3] carried out radiation graft copolymerization (by ionic mechanism) of 4VP onto LDPE, high density polyethylene, PTFE, and poly(vinyl chloride) films, discussing the possibility for simultaneous ionic and radical copolymerization. Other authors[7,10] studied the effect of monomer concentration on the grafting rate of 4VP and N-vinylpyrrolidone onto PTFE. Kaur and coworkers[11,12] investigated the radiation grafting of 4VP and binary mixture of 4VP and acrylonitrile onto isotactic polypropylene films and powders. Radiation grafting of 4VP onto polypropylene fibers and their functionalization with chromium trioxide has also been reported.[13] However, no systematic research has been reported either on radiation synthesis of the copolymers or on the phase composition of the copolymers. The effect of the hydrophilic phase of the grafted P4VP on the whole complex of properties of the copolymers and their fields of application are still under discussion.

In this respect, the aim of the present work is to study the synthesis, the structure, and some of the basic properties of the copolymers based on P4VP grafted onto LDPE and PTFE films.

EXPERIMENTAL

Films of LDPE RopotenT (product of Neftochim Co., Bourgas, Bulgaria) and PTFE (ONPO Plastpolymer, St. Peterburg, Russia), both 40 μm thick, were used as matrices for the grafting of the vacuum-distilled 4VP (product of Aldrich Chemical Co., Ltd., Gillingham, England). All other reagents used (methyliodide, methyl alcohol, nitromethane, etc.) were of analytical grade.

The polymer films (sized 150×200 mm) were cast with acetone and dried to constant mass at 333 K in a vacuum oven.

The graft copolymerization was carried out at 288 K in an inert (N_2) atmosphere by ^{60}Co γ-source in Pyrex glass reactors equipped with vacuum stopcocks at both ends. The polymer films were placed on a gauze filter plate at the bottom of the reactor, above the lower stopcock. With the lower stopcock closed, the reactors with films therein were evacuated to $10^{-3}–10^{-4}$ mmHg. Then 240 cm^3 40 mass % methanol solution of 4VP (purged in advance with N_2) was introduced through the lower stopcock. The whole system was purged with N_2 for 10 to 15 min, the two stopcocks were closed, and the reactors were placed in the γ-irradiator.

The direct method of multiple grafting was used within the interval of doses from 1 to 35 kGy (at dose rate of 3.5 kGy/h) at 288 K. Postpolymerization time was 2 h after each irradiation period at the same temperature. The number of irradiation periods (multiple irradiation) was determined by the integral dose. After irradiation the films were washed several times with methanol to remove the unreacted 4VP and homopolymer P4VP. The grafted copolymers were dried at 333 K in a vacuum oven to constant mass.

Infrared (IR) spectra of sample films were taken by using a Specord IR 75 spectrophotometer (Jena, Germany). The thermal and thermodynamic properties of the grafted copolymers synthesized were determined on a derivatograph type OD-102, system F. Paulik–J. Paulik–L. Erdey (MOM, Budapest, Hungary) and scanning calorimeter DSC-111 (Setaram, Lyon, France). The melting and crystallization temperatures (T_m and T_c, respectively) were determined by differential scanning calorimetry curves (exo- and endo-peaks) with the necessary temperature corrections.

The X-ray analysis was performed on TUR M62 apparatus (Jena, Germany) under the following conditions: CoK$_\alpha$ radiation, 32 kV, Fe filter, angle θ range from 5 to 30°. The degree of crystallinity α and crystallite size L_θ (Å) were calculated by fitting of the Gauss and Lorentz theoretical functions to the experimental X-ray patterns:

$$\alpha = \frac{S_c}{S_c + S_a} \times 100\%$$

where S_c and S_a are the areas of the crystalline peak and amorphous halo, respectively;

$$L_\theta = \frac{k\lambda}{\beta \cos \theta}$$

where λ is the wave length (Å) for Co anode; β is the difference between the half-widths of the diffraction maxima of the copolymer analyzed and the standard (rad); and k is the constant, equal to 0.9 for polymers.

The quaternization of the initial pyridine groups in the grafted copolymers into pyridinium was carried out by treatment with excess CH$_3$I in methanol medium (nitromethane at 315 K for 40

h). The AEM were swelled prior to the quaternization in a nitromethane/methanol medium.[14,15]

The grafting degree (P, %), water content (W, %), specific electric resistance (R, ohm cm), and transport number ($\bar{t}_-$) were determined by techniques described in previous works.[16–18] The diffusion coefficient (cm^2/s) was measured in $0.5M$ HCl and $0.5M$ HNO$_3$ at 298 K.[19] The thermal stability was determined at 343 K in air for a 48-h period of treatment.[20] The physicomechanical characteristics of wet AEM samples were measured on an Instron 4203 testing machine at 298 K at speeds of 5 and 100 mm/min (for PTFE) and 50 mm/min (for LDPE).

RESULTS AND DISCUSSION

By varying the reaction conditions of the radiation copolymerization, grafted copolymers were obtained with degrees of grafting (P) from 17.1 to 74.5% for LDPE and from 0.7 to 13.4% for PTFE. The method of multiple grafting used, involving postpolymerization effect, provides a possibility for the monomer to penetrate into the polymer matrix together with the stepwise generation of free radicals. As a result, the grafting proceeds within the polymer matrix, thus reducing the thickness of the nongrafted layer. This is crucial for the properties of the AEM obtained.

Figure 1 shows the dependence of the grafting degree of 4VP onto LDPE and PTFE films on the irradiation dose (D) in logarithmic coordinates. The dependence is linear and can be described by the relationship $P \propto D^n$, where $n_{\text{LDPE}} = 0.4$ and
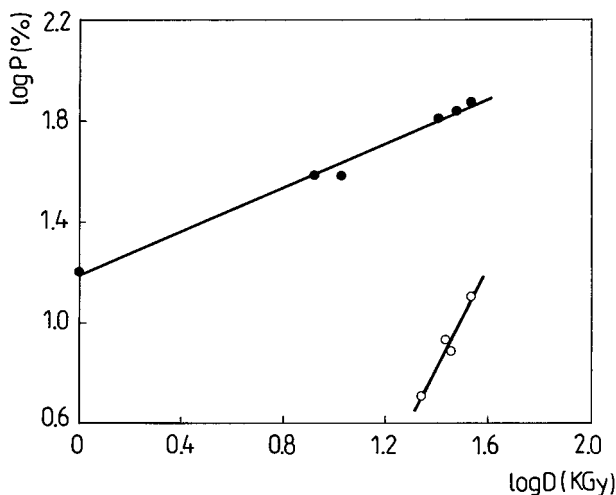

Figure 1 Dependence of the grafting degree of 4VP onto LDPE (●) and PTFE (○) on irradiation dose in logarithmic coordinates.
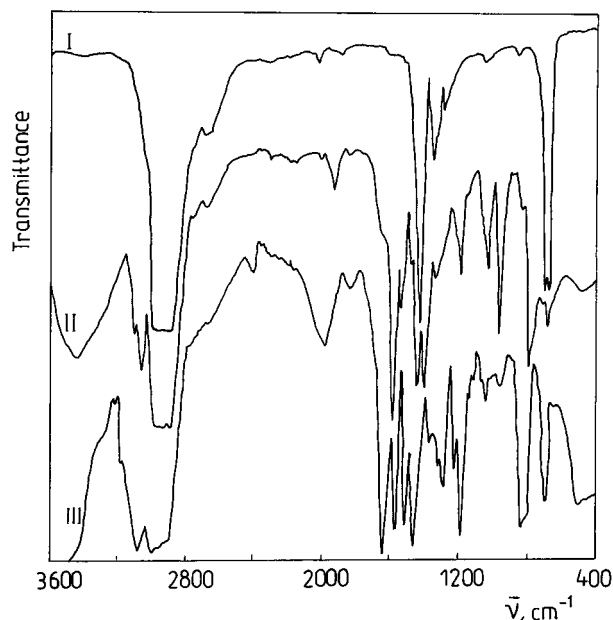

Figure 2 Infrared spectra of nongrafted LDPE (I), LDPE-g-P4VP (II) and LDPE-g-P4VP-CH$_3$I (III) with grafting degree of 74.5%.

$n_{\text{PTFE}} = 2.1$. It means that the irradiation exerts stronger effect on the grafting onto PTFE compared with that onto LDPE, which is connected with the lower radiation resistance of C—F compared with C—H bonds.

In the IR spectra of polyethylene-($graft$-poly-4VP) (LDPE-g-P4VP) (Fig. 2) and polytetrafluoroethylene-($graft$-poly-4VP) (PTFE-g-P4VP) (Fig. 3), absorption bands can be observed within the interval from 3000 to 3100 cm^{-1}, corresponding to $\nu(\text{=CH})$ vibrations of the pyridine nucleus. The absorptions observed at 1595 to 1600 cm^{-1} [corresponding to $\nu(\text{C=C})$ and $\nu(\text{C—N})$] also prove the presence of the pyridine nucleus. In the spectra of LDPE-g-P4VP and PTFE-g-P4VP quaternized with CH$_3$I, the bands at 1600 cm^{-1} are shifted to 1640 cm^{-1}. This is probably connected with the disturbance of the system of conjugated double bonds in the pyridinium nucleus. It should be noted also that the absorptions at 1000 to 1080 cm^{-1} corresponding to the valent vibrations of the conjugated $\left(\begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} C = C \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \right)$ bonds in the nucleus disappear, which means that the electronic charge is pulled from the iodine atom to disturb the conjugated system. The doublet at 728 cm^{-1} representing the crystal phase of LDPE turns to a singlet, which is probably due to partial amorphization of the polyethylene matrix as a result
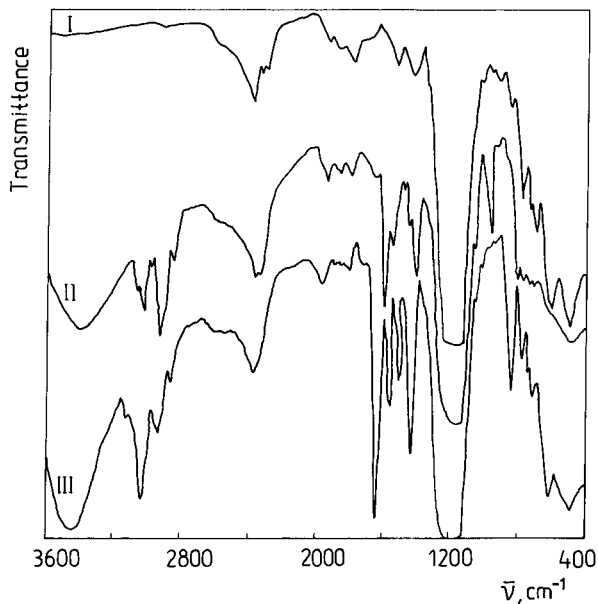
Figure 3 Infrared spectra of nongrafted PTFE (I), PTFE-*g*-P4VP (II) and PTFE-*g*-P4VP-CH₃I (III) with grafting degree of 13.4%.

of the grafting of 4VP. The intensity of this band increases with the degree of grafting.

Further studies on the structure of the grafted copolymers were carried out by X-ray analysis. The diffractions from the copolymer film were measured to investigate in detail the effect of the grafted P4VP on the polymer matrix.

Figure 4 shows the dependence of the degree of crystallinity (α) on the grafting degree; α decreases with the increase of P which is due to the growth of the amorphous phase of the copolymer with the increase in the grafted P4VP.

The size of the crystallites L_θ also decreased in proportion to the increase of P (Fig. 4), as the defectiveness of the crystallites increased (their perfection decreased) with the grafting which takes place probably in the folds of the polymer chains. It should be noted that sol–gel analysis of LDPE irradiated with the same doses (1–35 kGy) used for the grafting did not show processes of destruction or crosslinking. Therefore, the amorphization is caused only by the grafting. However, irradiated nongrafted PTFE films show higher crystallinity ($\alpha = 50\%$) compared with the initial film ($\alpha = 43\%$). It could be suggested that the irradiation of PTFE with small doses induces processes of destruction followed by recrystallization, resulting in an increased crystallinity. In PTFE films, as a result of the grafting, the crystallinity decreases sharply and

eliminates the increase in the crystallinity of nongrafted irradiated PTFE film.

Differential thermal analyses of LDPE-*g*-P4VP and PTFE-*g*-P4VP films showed that thermooxidative destruction occurs in two stages: primary, of the unstable fragments (grafted chains of P4VP); and secondary, of the main polymer chain (Table I). During the primary oxidative destruction, the destruction energy (E_d) decreases with the increase in the grafting degree. The thermal stability of the grafted copolymers decreases with the increase in P because of the increase in the share of the unstable pyridine groups. During the second stage, E_d depends on the nature of the initial polymer matrix and decreases to a higher extent for LDPE, while for PTFE it remains almost the same.

The enthalpies of melting and crystallization of the synthesized graft copolymers decrease with the increase in the grafting degree of 4VP (Table I), which is in accordance with the data from spectral and X-ray analyses. This, together with the slight increase in T_m and decrease in T_c of the P4VP grafted films, shows that the grafting takes place mainly in the amorphous phase, without changing the type of the crystalline structure of the polymer matrix.

The hydrophilization of the grafted polymer matrices was determined mainly by the concentration of the functional groups in the grafted copolymer. The latter stipulate the swelling of the membranes in water solutions under working conditions. Figure 5 shows that the water content of the AEM obtained increases linearly with the grafting degree of 4VP. The anionic polar groups were hydrated by water molecules to form associ-
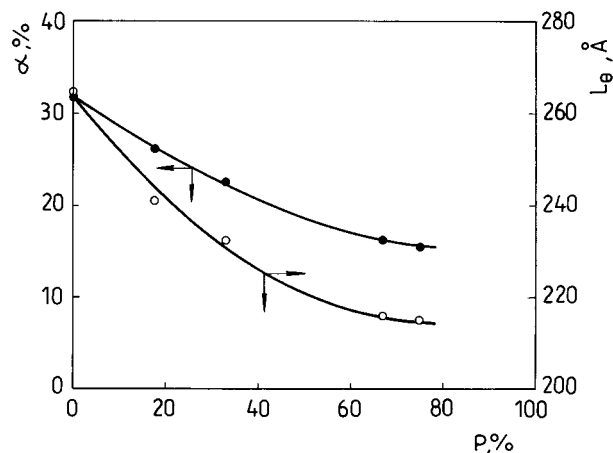

Figure 4 Dependence of the degree of crystallinity α (%) and crystallite size L_θ (Å) on the grafting degree of 4VP onto LDPE films.

4VP COPOLYMERIZATION ONTO PE AND PTFE **1473**

Table I Thermodynamic and Thermal Characteristics of Grafted Copolymers

Copolymer	Grafting Degree, P (%)	Thermodynamic				Primary Oxidative Destruction		Main Chain Destruction	
		T_m (K)	ΔH_m (J/g)	T_c (K)	ΔH_c (J/g)	ΔT (K)	E_d (kJ/mol)	ΔT (K)	E (kJ/mol)
LDPE-g-P4VP	0	377.5	96.0	376.3	78.0	493–646	—	613–778	220
	17.1	380.4	95.3	370.2	80.6	500–641	160	641–773	210
	32.6	382.4	62.5	370.2	53.5	495–621	124	621–775	184
	67.1	381.4	50.0	370.2	51.5	495–627	91	627–774	173
	74.5	381.4	46.8	366.2	41.5	494–684	58	684–771	153
PTFE-g-P4VP	0	600.1	58.0	594.6	57.0	—	—	763–864	
	8.9	603.9	46.7	590.6	44.9	522–634	225	634–853	300 ± 20
	13.4	603.9	44.2	586.6	41.4	548–650	218	650–863	

ates with ionic channels. The hydrophobic hydro- or fluorocarbon components and the hydrophilic ionic groups are incompatible. Therefore, separation of their phases takes place, leading to formation of internally bonded hydrated ionic clusters which determine the electrochemical properties of the membrane. The hydrophobic phase controls the swelling and does not allow the dissolution of the ionic phase. The amount of water in the membrane is crucial for selectivity—a very high swelling decreases the selectivity. Therefore, an optimum should be found to obtain a membrane

Figure 5 Dependence of the water content W (%) of AEM on the grafting degree P (%) of 4VP onto LDPE (●) and PTFE (○) films.

of good mechanical and electrochemical properties and high selectivity.

In order to obtain membranes of certain hydrophilicity, the initial membranes were quaternized by treatment with excess CH_3l. The transformation of the pyridine groups into strong basic pyridinium groups increased the polarity of the C—N bond because the tertiary N atom becomes quaternary and also increases the AEM hydration.

The thickness of the grafted layer of P4VP affects the values of the specific electric resistance. The latter decreases with the increase in the amount of grafted P4VP (Table II) and for ionomers based on LDPE was found to be from 10^2 to 10^3 ohm cm. Hence, the membranes have low electric resistance ($R \leq 10^4$ ohm cm)[21] and they are suitable for preparation of AEM. For PTFE, as it is an excellent dielectric, the grafting of 4VP led to a decrease in R from 10^{19} ($P = 0\%$) to 10^5 ($P = 13\%$) ohm cm, but it is still high enough. Unfortunately, higher grafting degrees onto PTFE are very difficult to obtain because of its low swelling and the low diffusion of 4VP into the PTFE matrix.

We also studied the diffusion of inorganic acids through the grafted membranes. The diffusion direction in this case was determined by the anions, since the hydrogen ion has very high diffusion coefficient due to its small size.[19]

The diffusion coefficients of the synthesized membranes, presented in Table II, show that diffusion depends on the grafting degree and varies from 2.0×10^{-8} to 6.6×10^{-7} cm^2/s for LDPE-g-P4VP-CH$_3$I and from 6.0×10^{-8} to 5.8×10^{-7} cm^2/s for PTFE-g-P4VP-CH$_3$I. Thus they are suitable for use in electrodialysis processes.[19]

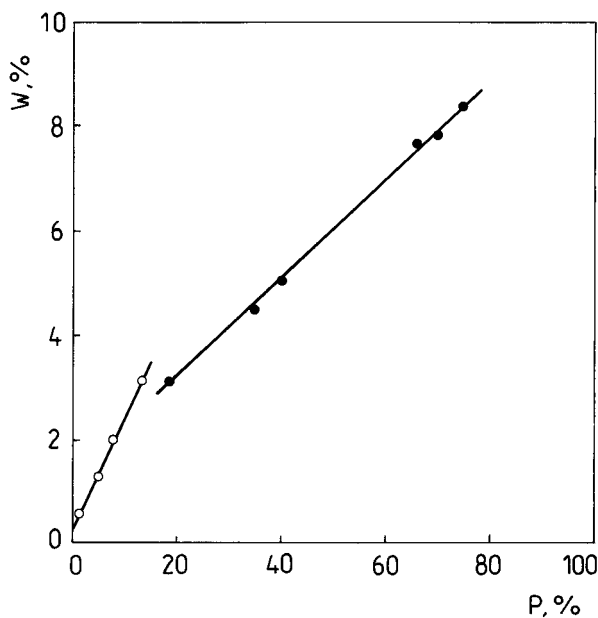Figure 6 shows the dependence of the transport

Table II Dependence of the Specific Electric Resistance and Diffusion Coefficients of AEM in Pyridinium Form on the Grafting Degree of 4VP onto LDPE and PTFE

AEM	Grafting Degree (%)	Specific Electric Resistance (ohm cm)	Diffusion Coefficient (cm²/s)	
			HCl ($\times 10^7$)	HNO$_3$ ($\times 10^8$)
LDPE-g-P4VP-CH$_3$I	0	1.0×10^{12}	—	—
	18.2	9.5×10^3	1.7	2.0
	35.1	1.9×10^3	2.1	5.8
	39.3	1.5×10^3	2.4	7.4
	66.2	9.5×10^2	4.4	8.0
	69.8	8.0×10^2	6.0	8.3
	74.5	7.1×10^2	6.6	9.2
PTFE-g-P4VP-CH$_3$I	0	1.0×10^{19}	—	—
	0.7	6.4×10^8	—	—
	6.5	9.5×10^7	—	—
	8.2	7.9×10^5	—	—
	13.4	1.1×10^5	5.8	6.0

number $\bar{t}_-$ of the membranes synthesized in pyridinium form on P. It has a maximum ($0.92-0.98$) between grafting degrees from 5 and 25%, depending on the type of the membranes. Above 25% P exerts only an insignificant effect on $\bar{t}_-$. This is probably determined by the decrease of the fixed ions concentration in the membranes obtained with the increase of the concentration of the ion-exchange groups.

The thermal stability at higher temperature is an important characteristic of the ion-exchange membranes, since in a number of cases the electrodialysis processes are carried out in a heated electrolyte. The thermal stability of AEM in pyridine and pyridinium forms and with different grafting degrees is quite good (the weight loss is $\leq 1.5\%$).
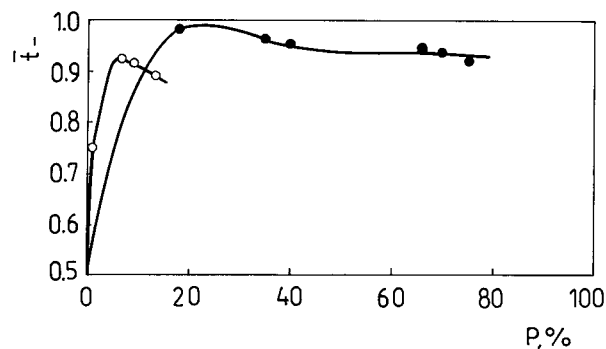
In order to determine the resistance of the AEM

Figure 6 Dependence of the transport number ($\bar{t}_-$) of AEM on the grafting degree P (%) of 4VP onto LDPE ($\bullet$) and PTFE ($\bigcirc$) films.

to mechanical stress, their tensile properties were studied in both forms. Since AEM are used in water solutions, these characteristics were determined by using membranes swollen in water to equilibrium.

Table III shows the tensile strength (σ) and elongation at break (ϵ) of the membranes synthesized in both forms. For membranes based on LDPE (in both forms), σ shows a maximum for grafting degrees from 25 to 40% and ϵ decreases. The tensile characteristics of AEM based on PTFE decrease with the increase of the grafting degree. This effect is probably caused by processes of radiation destruction occurring in the initial polymer matrix at higher grafting degrees.

The tensile properties of LDPE-g-P4VP at grafting degrees from 20 to 40% seem to be suitable for application without additional reinforcement. The elasticity of PTFE-g-P4VP membranes significantly decreases, however, which limits their use as self-supporting membranes.

CONCLUSION

Grafted copolymers were obtained by radiation graft copolymerization by using the multiple grafting of 4VP onto LDPE and PTFE films. The grafting degree of 4VP can be described by the relationship $P \propto D^n$, where $n_{\text{LDPE}} = 0.4$ and $n_{\text{PTFE}} = 2.1$. The structure of the copolymers obtained was studied by several physical methods. A two-stage thermooxidative destruction was observed,

Table III Tensile Properties of Aquagels of AEM in Pyridine and Pyridinium Forms

Grafting Degree (%)	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Elongation at Break (%)
	LDPE-*g*-P4VP		LDPE-*g*-P4VP-CH$_3$I	
0	18	319	—	—
18.3	16	297	33	360
39.2	22	286	34	217
69.0	25	267	29	214
74.5	24	204	32	203
	PTFE-*g*-P4VP		PTFE-*g*-P4VP-CH$_3$I	
0	25	170	—	—
0.7	21	30	17	37
6.5	18	10	15	7
8.2	—	—	14	5
12.4	19	7	6	3

as well as a decrease in the degree of crystallinity with the increase in the grafting degree.

Quaternization of AEM synthesized was carried out and some of their basic properties were studied. The swelling in water depends linearly on the amount of grafted functional monomer. The thickness of the grafted layer of P4VP significantly affects the electrochemical, thermal, and tensile properties of the grafted membranes obtained. The membranes possess a good complex of properties at grafting degrees from 20 to 50% for LDPE-*g*-P4VP and up to 13% for PTFE-*g*-P4VP. They can be used together with the carboxyl-containing cation-exchange membranes synthesized earlier[22] in various electrodialysis processes, for water desalination and purification.

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