

Investigation of Radiation-Grafted and Radiation-Modified *N*-Vinyl-2-pyrrolidone onto Polypropylene Film

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Received 6 January 1999; accepted 6 June 1999

ABSTRACT: The radiation-induced graft copolymerization of *N*-vinyl-2-pyrrolidone (NVP) onto polypropylene films was investigated using the mutual method. The grafted polymer was modified with prepared α,β -unsaturated nitrile (Scheme 1). The water uptake of the grafted and modified grafted films was found to increase with the degree of grafting. It was observed that the swelling behavior of the modified grafted films with α -cyano- β -phenyl crotononitrile improved more than that of the film grafted and modified grafted with α -cyano- β -(2-thienyl)crotononitrile or α -cyano- β -(2-pyridyl)crotononitrile. The modification process for the grafted substrate was confirmed by IR spectroscopy. No significant improvement was observed in thermal stability for the modified grafted films compared to the grafted films. Scanning electron microscopy (SEM) of the grafted and modified grafted membranes heated to 150°C showed change in the structure and morphology. Improvement in the hydrophilicity and morphology of these membranes with carbonitriles may increase the permeability of those membranes for some practical applications. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 282–289, 2000

Key words: graft copolymerization; NVP; carbonitrile; hydrophilic; morphology

INTRODUCTION

Radiation-induced graft copolymerization is a well-known important method for modification of the chemical and physical properties of polymeric substrate. Also well known is the use of *N*-vinyl-2-pyrrolidone (NVP) as a hydrophilic graft monomer in radiation grafting on various trunk polymers, and it has been described as useful not only for the preparation of biocompatible polymer surfaces¹ but also for the preparation of membranes.^{2–8} The water-absorption capacity of grafted and modified membranes is directly related to the degree of crosslinking, which itself depends greatly on the radiation dose. Consequently, the graft copolymerization of NVP onto

various polymers is widely used in biomedical applications because of its excellent biocompatibility and high water permeability.⁹ The surface structures and morphology of trunk polypropylene (PP) or grafted PP with 2-hydroxyethyl methacrylate (HEMA) were also investigated.¹⁰ The thermal behavior of the copolymer of NVP with acrylamide (Am) was also examined,¹¹ as well as modification of radiation graft polymerization of NVP onto low-density polyethylene (LDPE) with α,β -unsaturated nitrile for biological activity.^{8,12–16}

This article reports on the study and analysis by the measurement of monomer concentration and by IR spectroscopy of direct radiation grafting of NVP onto PP. The grafted and modified copolymers were investigated by elemental analysis, scanning electron microscopy (SEM), and thermogravimetry (TG).

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Journal of Applied Polymer Science, Vol. 76, 282–289 (2000)
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EXPERIMENTAL

Materials

Used as a polymer substrate was 35- μm -thick polypropylene (PP) film (El-Nasr Co. for medical supplies, Egypt). *N*-vinyl-2-pyrrolidone (NVP) 99% pure (Merck, Germany) was used without further purification. The α,β -unsaturated nitrile compounds (**2a–c**, Scheme 1) were prepared as described earlier.¹⁷ Other chemicals were of reagent grade and were used without further purification.

Graft Polymerization

Strips of PP were washed with acetone, dried in a vacuum oven at 50°C, weighed, and immersed in the monomer-dimethyl formamide (DMF) solution in glass ampoules. Ferric chloride (0.008%)⁸ was added to the monomer–solvent mixture to reduce the homopolymerization process during irradiation. The glass ampoules that contained polymer and monomer–solvent mixtures were de-aerated by the bubbling of nitrogen gas for 5–7 min, sealed, and subjected to ⁶⁰Co γ source at a dose rate of 1.60 Gy/sec. The obtained grafted films were removed and washed thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and homopolymer occluded in the film. The grafted films were then dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting was determined by the percentage increase of weight as follows:

$$\% G = \frac{W_g - W_0}{W_0} \times 100$$

where W_g and W_0 represent the weight of the grafted and the initial films, respectively.

Preparation of the Modified Grafted Films with α,β -Unsaturated Nitrile

Colorless grafted films (3 \times 3 cm) were immersed in a solution prepared from **2a–c** (~5 g) and a few pellets of sodium hydroxide (~0.5 g) in ethanol (50 mL). The resulting mixtures were refluxed for 36 h. The colored films (brown to dark brown) were removed and washed with distilled water and ethanol, followed by drying over filter paper.

Swelling Measurements

The clean, dried polypropylene-g-poly(*N*-vinyl-2-pyrrolidone) (PP-g-PVP) and modified films with

α,β -unsaturated nitrile were immersed in distilled water for 24 h. The films were removed, blotted, and immediately weighed. The swelling percent was calculated as follows

$$\text{Swelling \%} = \frac{W_s - W_g}{W_g} \times 100$$

where W_g and W_s represent the weight of the initial modified grafted and the swelled modified grafted films, respectively.

General Method for Preparation of Crotononitrile Derivatives (**2a–c**)

To a mixture of benzene (20 mL), acetic acid (0.01 mol), and ammonium acetate (0.01 mol) was added acetyl thiophene or acetyl pyridine or acetophenone (0.01 mol) and malononitrile (0.01 mol). The mixture was heated 10–15 min and then left overnight. The solid product formed on the addition of 20 mL of ethanol was collected by filtration, washed with cold water, and then crystallized from a proper solvent.

α -Cyano- β -(2-thienyl)crotononitrile (**2a**)

Compound (**2a**) formed as yellow needle crystals (1.48 g, 85%) of m.p. 88–90°C (from ethanol). $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 2210, 2220 cm^{-1} . δ_H 8.24–8.05 (dd, 2 H, thienyl), 7.42–7.31 (*t*, 1 H, thienyl), 2.68 (*S*, 3 H, CH₃). Elemental analysis for C₉H₆N₂S, found: C, 61.77; H, 3.40; N, 15.89; S, 18.10; calcd: C, 62.03; H, 3.47; N, 16.07; S, 18.40.

α -Cyano- β -(2-pyridyl)crotononitrile (**2b**)

Compound (**2b**) formed as brown crystals (1.38 g, 82%) m.p. 110–112°C (from ethanol). $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 2203 cm^{-1} . δ_H 8.92–6.90 (4 H, pyridyl), 2.61 (*S*, 3 H, CH₃). Elemental analysis for C₁₀H₇N₃, found: C, 71.23; H, 4.32; N, 24.56; calcd: C, 70.99; H, 4.17; N, 24.82.

α -Cyano- β -phenyl crotononitrile (**2c**)

Compound (**2c**) formed as yellow needles (1.44 g, 86%) m.p. 86–88°C (from ethanol). $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 2225 cm^{-1} . δ_H 7.9–7.2 (*m*, 5 H, phenyl), 2.62 (*S*, 3 H, CH₃). Elemental analysis for C₁₁H₈N₂, found: C, 78.32, H, 4.78, N, 16.64 calcd: C, 78.55, H, 4.79, N, 16.65.

Infrared Spectroscopy

Infrared spectra were measured for the trunk, grafted, and modified grafted PP films, using a Shimadzu 5000 FTIR spectrometer (Japan).

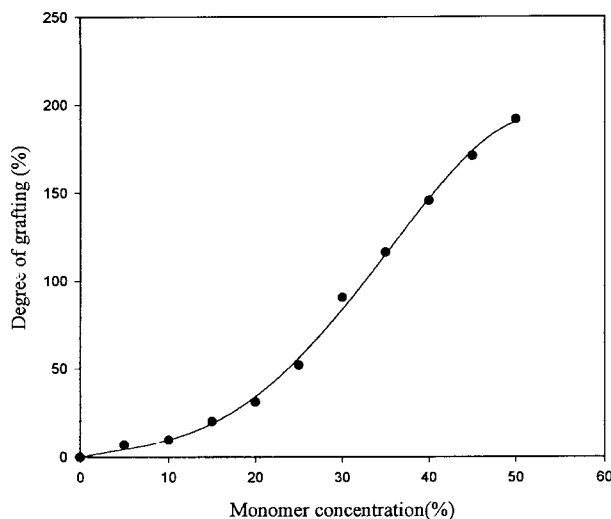


Figure 1 Degree of grafting of PP as a function of monomer concentration (NVP). Grafting conditions: NVP, diluent, DMF, FeCl_3 as inhibitor (0.008 wt %), nitrogen atmosphere (5–7 min) at room temperature, Irradiation dose: 20 kGy.

Thermogravimetry

Thermogravimetry (TG) curves were obtained on heating test materials (at $20^\circ\text{C}/\text{min}$) in a dynamic atmosphere (30 cc/min) of pure nitrogen gas by means of a Shimadzu DSC 50 analyzer (Japan).

Scanning Electron Microscopy (SEM)

The grafted and modified grafted copolymers were examined in a model JSM-6300 JEOL scanning electron microscope (SEM) at 20 kV.

RESULTS AND DISCUSSION

Effect of NVP Concentration

Figure 1 shows that the degree of grafting increases gradually with NVP concentration in DMF (dimethyl formamide) and FeCl_3 (0.008 wt %) as inhibitor at 20 kGy. The presence of DMF and FeCl_3 has been effected on the grafting reaction to enhance monomer concentration through the polymer matrix with the reducing of the homopolymer of monomer during the irradiation process. Therefore, it is apparent that the solvent-inhibitor mixture permits attainment of much higher grafting levels as NVP increases.

This result suggests that the degree of grafting is dependent not only on the formation of active sites due to irradiation grafting, but also on the

diffusivity of NVP in the PP membrane. The diffusibility of monomer may enhance the grafting yield upon increasing of monomer concentration.

IR Spectroscopic Investigation of Grafted and Modified Copolymers

Figure 2 shows that the IR spectra for the original PP (curve a), for PP-g-PVP (curve b), and for its

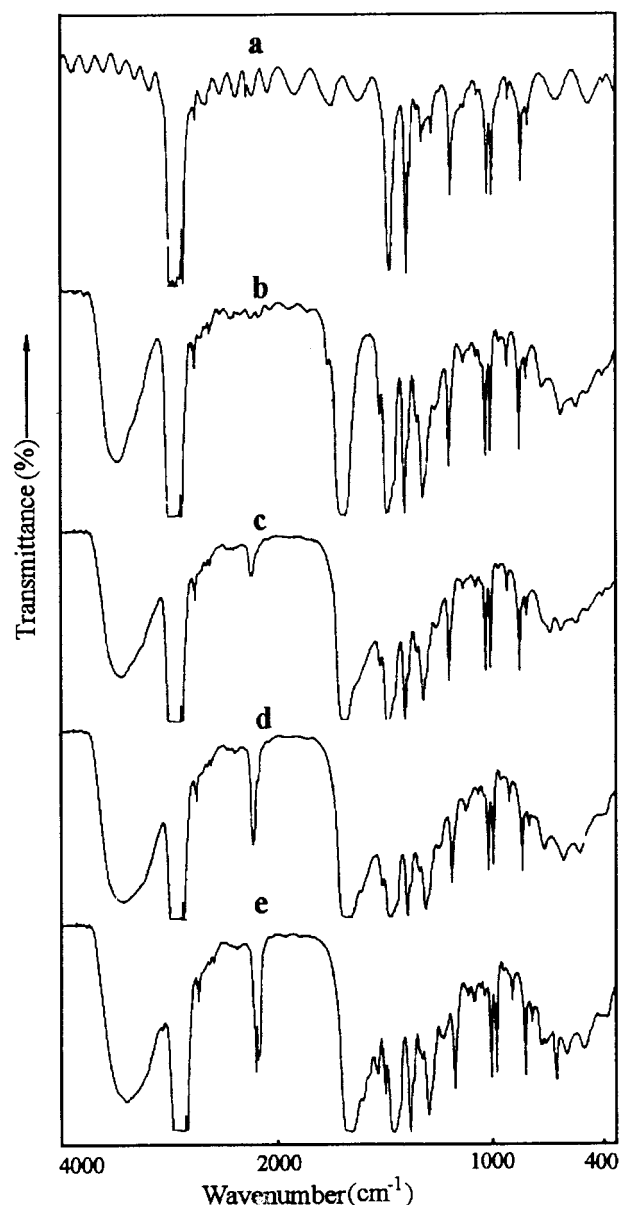


Figure 2 IR spectra of original PP (curve a), PP-g-PVP (curve b), PP-g-PVP modified with α -cyano- β -(2-thienyl)crotononitrile (curve c), PP-g-PVP with α -cyano- β -(2-pyridyl)crotononitrile (curve d), and PP-g-PVP with α -cyano- β -phenyl crotononitrile (curve e), all having the same degree of grafting (25.9 wt %).

Table I Elemental Analysis of the Grafted and its Modified Grafted 3(a-c) at 25.9 wt % and 52.9 wt % Grafting

Compound No.	% G	% C	% H	% N	% S
1	25.9	76.00	13.42	2.02	0.00
	52.9	73.30	12.50	4.05	0.00
3a	25.9	76.88	12.64	1.70	1.26
	52.9	72.44	11.31	4.24	1.93
3b	25.9	75.74	13.26	3.05	0.00
	52.9	72.49	12.21	5.34	0.00
3c	25.9	77.84	11.73	2.79	0.00
	52.9	72.73	11.13	5.57	0.00

modified grafted copolymer with crotononitrile derivatives (curves c–e) have the same degree of grafting (25.9 wt %). It can be seen (curve a, Fig. 2) that bands appearing at 2840–2800, 1440, and 1380 cm^{-1} are characteristic for the PP structure. However, in the case of PP grafted with NVP (curve b, Fig. 2), the bands appearing at 3429 cm^{-1} and 1659 cm^{-1} are attributed respectively to $\nu(\text{OH})$ of water contamination and $\nu(\text{C}=\text{O})$ of amide group.¹⁸ The intensity of the band at 1659 cm^{-1} is shown to increase with the grafting yield.

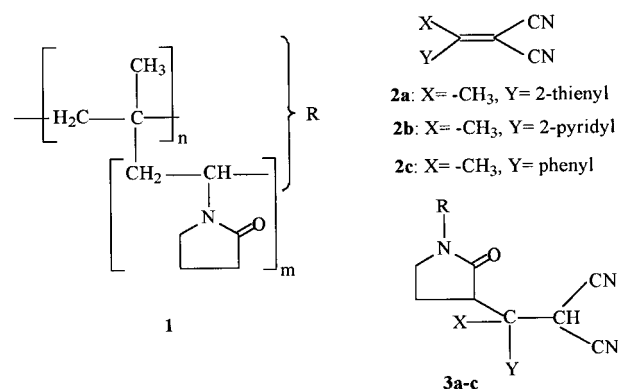
NVP can be viewed as a species containing three active sites: a vinyl group, a carbonyl group, and an active methylene function. These sites were reduced to two sites only following grafting. The remaining two sites, a carbonyl group and a methylene function, show a variety in the reactivity. The amide carbonyl group shows no reactivity toward the nucleophilic reagent, and this may be due to the lowest reactivity in the amide carbonyl group or may be due to the chain steric effect. The result prompted us to investigate the reactivity of the α -methylene function.

Compounds **2a–c** undergo a Michael addition reaction to give **3a–c**, (cf. Scheme 1), which is established not only by the IR spectra but also on basis of the elemental analysis results for the modified grafted reactions. The presence of sulfur (**3a**) and nitrogen in increasing amounts (**3b–c**) can be seen by comparing the data with the grafted membrane 1 in Table I. It can also be observed (Table I) that the modified grafted films **3a–c** increase the amount of sulfur and nitrogen based on the degree of grafting.

The modified grafted copolymer films **3a** (curve c, Fig. 2), **3b** (curve d, Fig. 2), and **3c** (curve e, Fig. 2) reveal the presence of cyano groups at 2195–2191 cm^{-1} , which were absent in the PP-g-PVP

(curve b, Fig. 2). Compound **3c** (curve e, Fig. 2) exhibits two IR bands at 2191 and 2169 cm^{-1} due to cyano groups, which were absent in the grafted films. The characteristic absorption of a carbonyl group appeared at 1659 cm^{-1} in addition to the absorption of the carbon–carbon double bond of the phenyl ring at 1528 cm^{-1} and that of C–N at 1218 cm^{-1} .

Compounds **3a–c** were believed to produce through the Michael addition of active methylene in **1** to an ethylenic double bond in **2a–c** as follows (Scheme 1):



Swelling Behavior of the Grafted and Modified Materials

Figure 3 shows the water uptake percent as a function of degree of grafting for PP-g-PVP (curve a) and for its modifications (curves b–d) with crotononitrile derivatives **2b**, **2a**, and **2c** to give **3b**, **3a**, and **3c** (cf. Scheme 1), respectively. It can be seen that water uptake increases with grafting yield for both the grafted and the modified grafted ones. Figure 3 generally shows that water uptake of modified grafted films is higher than that for the grafted ones at the same degree of grafting. However, the swelling behavior of the modified grafted **3c** (curve d, Fig. 3) is more obvious than that of the modified grafted **3b** (curve b, Fig. 3) or **3a** (curve c, Fig. 3). Also, it can be observed that the swelling of modified grafted **3a** (curve c, Fig. 3) is higher than that of the modified grafted **3b**, (curve b, Fig. 3).

The results suggest that water uptake increases in the grafted films due to inclusion of the electrolytic groups of the pyrrolidone ring, since PVP graft chains are hydrophilic in nature. Consequently, the swelling behavior of such a graft copolymer (curve a, Fig. 3) possessed good hydrophilic properties that increased with the grafting yield. However, the introduction of new rings

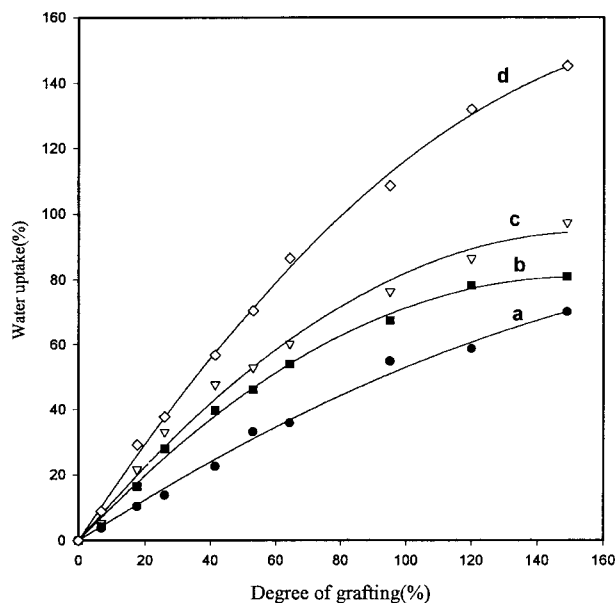


Figure 3 Percent of water uptake versus degree of grafting for PP-g-PVP (curve a), PP-g-PVP with α -cyano- β -(2-pyridyl)crotononitrile (curve b), PP-g-PVP with α -cyano- β -(2-thienyl)crotononitrile (curve c), and PP-g-PVP with α -cyano- β -phenyl crotononitrile (curve d), all having the same degree of grafting (52.9 wt %).

such as phenyl, thiophene, or pyridine in addition to the pyrrolidone ring through the backbone of polymer matrix may increase the hydrophilicity of these membranes than that of the grafted one. The electronegativity of the nitrogen atom in pyridine rings of modified grafted **3b** (curve b, Fig. 3) is more than the sulfur in the thiophene ring of the modified grafted **3a** (curve c, Fig. 3). Therefore, the hydrophilicity of the modified grafted **3b** (curve b, Fig. 3) is lower than that of the modified grafted **3a** (curve c, Fig. 3) membrane. Accordingly, the addition of a phenyl ring through the grafted polymer substrate may possess higher hydrophilicity because of its lower electronegativity. Therefore, the sequence of swelling behavior for the treatment of grafted films was found to follow the following descending order: curve (d) > curve (c) > curve (b) > curve (a), that is, compound **3c** > **3a** > **3b** > **1** (cf. Scheme 1).

Thermal Stability Measurements

Figure 4 illustrates the TG curves for trunk PP polymer substrate (curve a) and PP-g-PVP (curves b and c) at the grafting yields of 25.9% and 120%, respectively. It shows that the grafting process brought about increases in thermal sta-

bility with an increasing degree of grafting. Meanwhile, no significant improvement was observed in the thermal stability due to the addition of α,β -unsaturated nitrile compounds (**2a-c**) as compared with that of the grafted membranes.

The results showed that the increase in thermal stability for the graft copolymer having PVP graft chains may be due to the enhancement of crosslinking formation by poly(*N*-vinyl-2-pyrrolidone) (PVP) graft chains. However, no significant improvement was observed in the thermal stability of the modified films with crotononitrile derivatives, which may be due to the presence of a very low concentration of nitrile compounds through the polymer matrix of grafted chains.

Morphology

Figure 5 shows that the morphologies of heated (150°C) and unheated trunk PP and PP-g-PVP membranes observed by SEM have the same degree of grafting (52.9%). Both the heated and unheated PP membranes were found to be transparent. The SEMs of PP substrate before and after heating are shown in Figure 5(a-b). Figure 5(b) shows some change in the morphology due to heating. However, the presence of some distinct

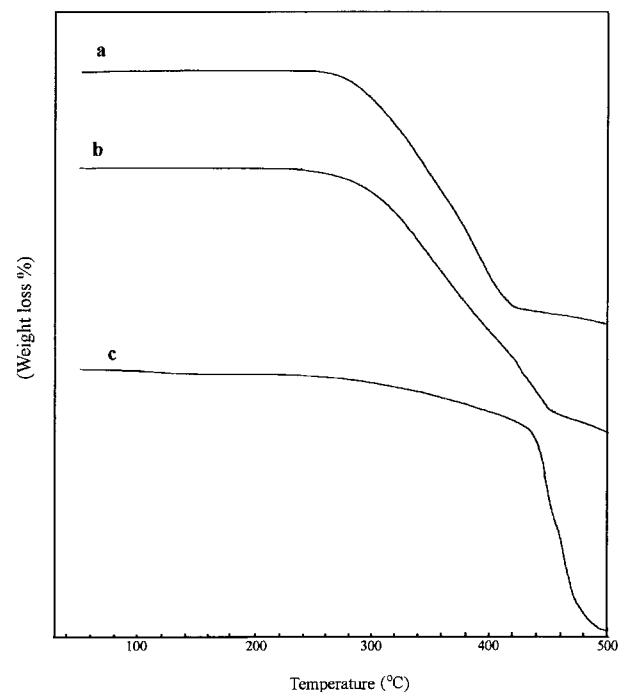


Figure 4 TG curves for the trunk PP (curve a) and PP-g-PVP (curves b and c) at degree of grafting of 25.9 wt % and 120 wt %, respectively.

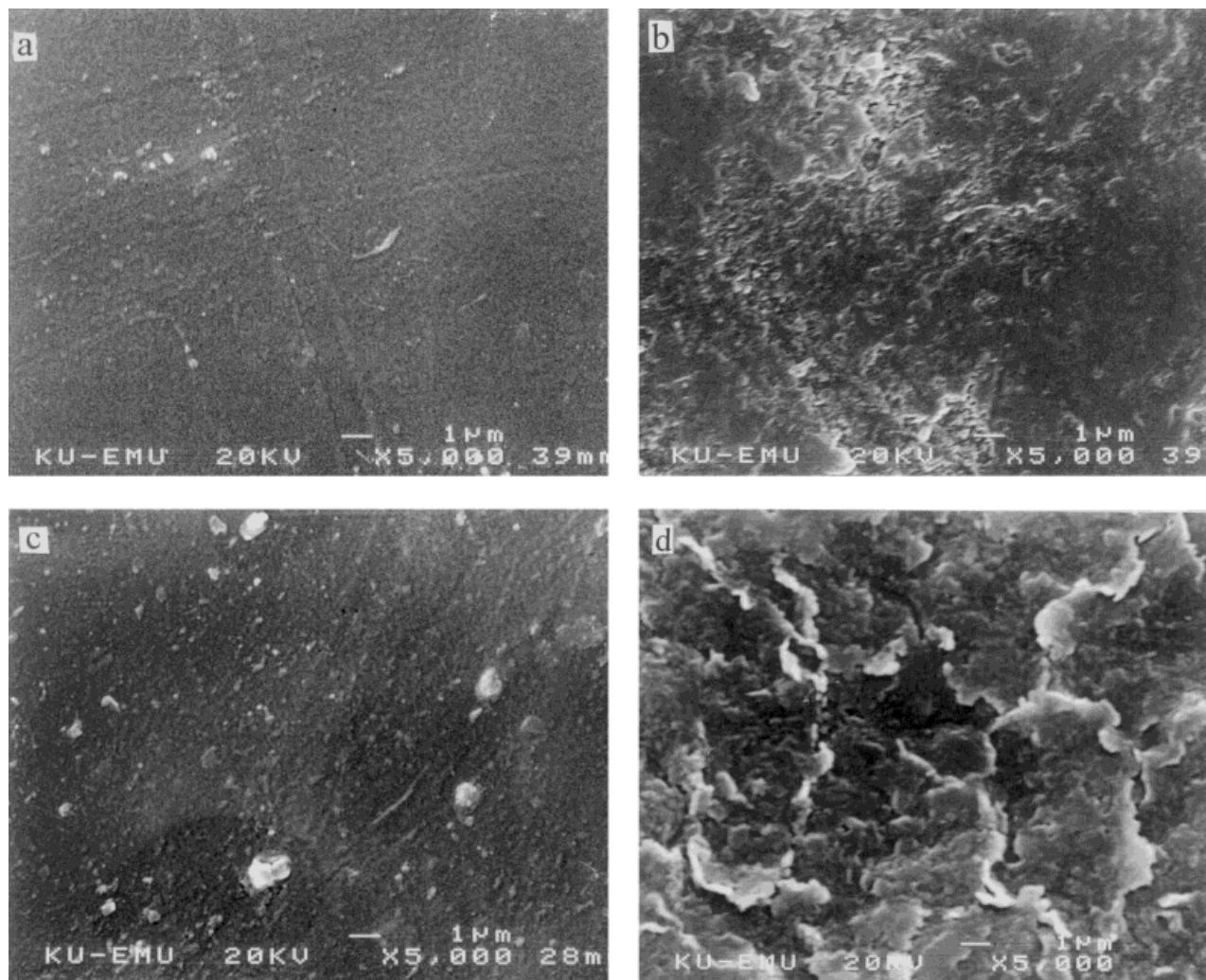


Figure 5 Scanning electron micrographs of the trunk PP (a and b) and PP-g-PVP (c and d) of the same degree of grafting (52.9 wt %), where (a) and (c) are for the unheated samples and (b) and (d) are for the 150°C heated samples.

spheres in the grafted films at room temperature [Fig. 5(c)] is due to embedding of PVP chains in the matrix of PP. The surface of the grafted membranes following heating to 150°C appears more crystalline in the grafted layer [Fig. 5(d)]. The grafted polymer exposed to a temperature of 150°C will rearrange the grafted layer on the surface of that membrane. Consequently, the amorphous region throughout the copolymer matrix may be changed, and the crystallinity should increase with elevating temperature.

The scanning electron micrographs depicted in Figure 6 show that the modified grafted PP with α -cyano- β -(2-pyridyl)crotononitrile [Fig. 6(a–b)], with α -cyano- β -(2-thienyl)crotononitrile [Fig. 6(c–

d)], and with α -cyano- β -phenyl crotononitrile [Fig. 6(e–f)] all have the same grafting yield (52.9 wt %) before and after heating at 150°C. It can be seen that the unheated modified grafted film [Fig. 6(a)] appears to have spheres as distinct as the grafted one [Fig. 5(c)]. Meanwhile, the heated membranes appear to be regular gatherings similar to a colony of microorganisms. In addition, the modification of unheated grafted films with α -cyano- β -(2-thienyl)crotononitrile [Fig. 6(c)] exhibits a rough morphology, while the heated membranes [Fig. 6(d)] assume a crystalline appearance, which may be due to the presence of the excited sulfur of the thiophene ring in the modified structure. The treated grafted membranes with α -cyano- β -phenyl crotononitrile [Fig. 6(e)]

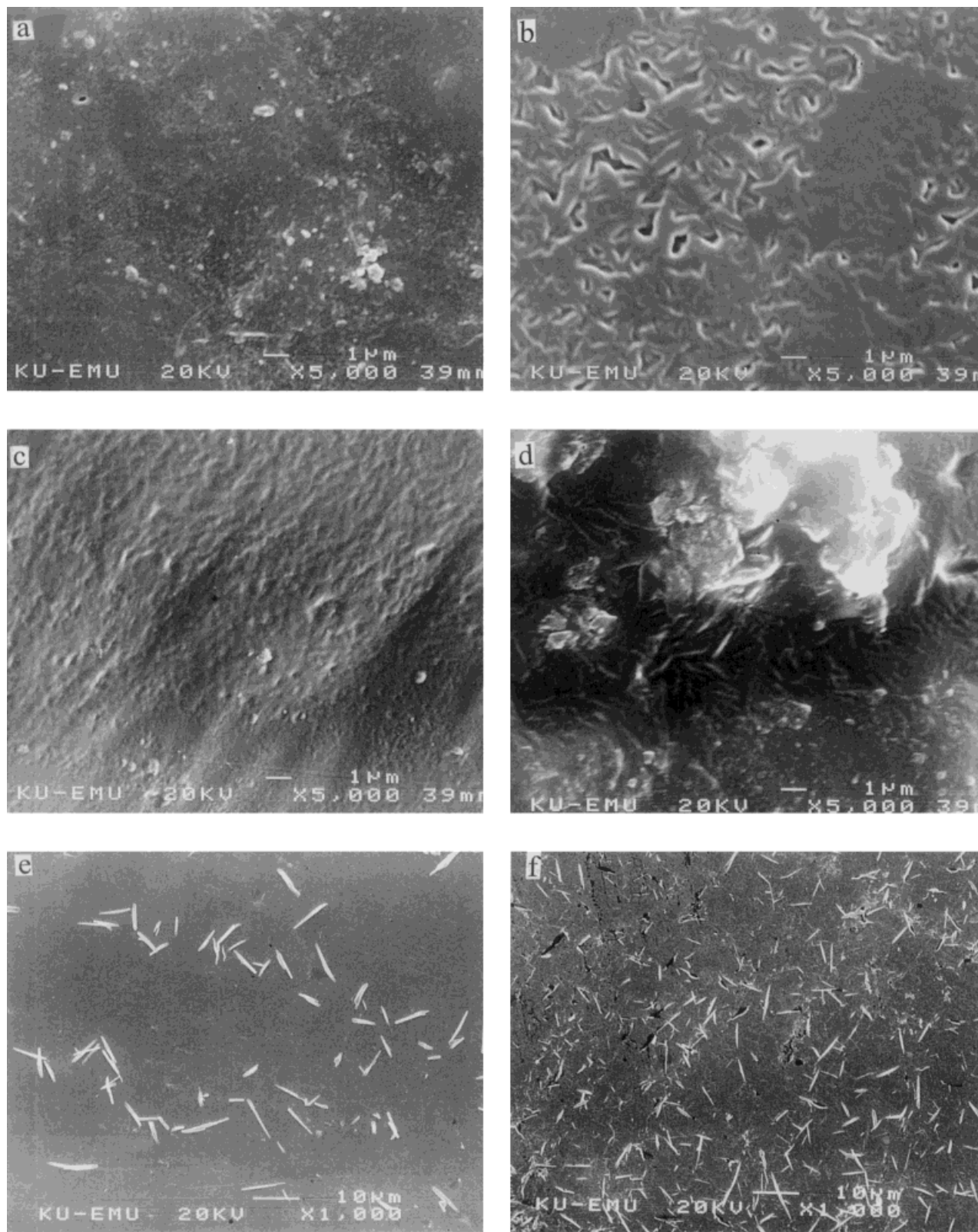


Figure 6 Scanning electron micrographs of the PP-g-PVP modified with α -cyano- β -(2-pyridyl)crotononitrile (a and b), α -cyano- β -(2-thienyl)crotononitrile (c and d), or α -cyano- β -phenyl crotononitrile (e and f) of the same grafting yield (52.9 wt %) where (a), (c), and (d) are for the unheated samples and (b), (d), and (f) are for the 150°C heated samples.

assume the appearance of needle-shaped crystals, which increase with heating [Fig. 6(f)].

The results suggest that the embedding of carbonitrile derivatives in the matrix of the grafted membranes increased with the degree of grafting.^{19,20} The surfaces of modified grafted membranes are translucent and smooth. Generally, the morphology changed as the temperature increased.¹⁰ Consequently, the crystallinity of the membranes may also increase.

The authors are grateful to the National Centre for Radiation Research and Technology, Nasr City, Cairo, Egypt, for preparation of the grafted films. The excellent technical assistance provided at the Analab/EMU/SAF of the Faculty of Science, Kuwait University, is highly appreciated.

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