

Recent Developments in the Radiation Grafting of *N*-Vinyl-2-pyrrolidone onto Low-Density Polyethylene with Cinnamitrile Derivatives

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ABSTRACT: The radiation-induced graft polymerization of *N*-vinyl-2-pyrrolidone onto low-density polyethylene films was conducted with γ radiation by a simultaneous technique. The grafted copolymer was modified with cinnamitrile or benzylidene malonitrile. The modified and grafted films were amidoximated with hydroxylamine hydrochloride in a basic medium. However, during amidoximation, the benzylidene malonitrile was cyclized to yield isoxazole ring through an addition to the nitrile group in its structure, whereas the nitrile groups of cinnamitrile were converted into amidoxime groups. The swelling behavior of the grafted copolymers and copolymers grafted and modified either with cinnamitrile or benzylidene malonitrile was studied. Amidoximated and grafted films and copolymer-metal complexes of Cu(II) were prepared and characterized. The effect of the isoxazole ring on polymeric materials was also investigated. These films were characterized with different analysis techniques, such as infrared, ultraviolet

(UV), elemental analysis, energy-dispersive spectroscopy, and electron spin resonance (ESR). The UV and ESR analyses revealed that the geometric structure of Cu(II) was square-planar. Scanning electron microscopy was used to examine the grafted and modified films to determine the changes in the surface morphology. Morphological changes clearly appeared for both complexed and isoxazole films because of the increase in their crystallinity. The thermal stability of different films was investigated with thermogravimetric analysis. The improvement of the copolymer by modification with cinnamitrile derivatives showed great promise for some practical applications, such as metal recovery by complexation or the use of isoxazole in medicine. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1189–1197, 2005

Key words: polyethylene (PE); radiation; graft copolymer; morphology

INTRODUCTION

Graft polymerization can be initiated by various methods, such as γ rays, electron beams, ultraviolet (UV), plasma treatment, and chemical initiators. Among these methods, ionizing radiation is one of the most promising because of its creation of active sites for initiating grafting through the matrix of a polymeric substrate and its moderate reaction conditions. Therefore, radiation grafting is a convenient method for the modification of physical and chemical properties of polymeric materials. The direct radiation grafting of *N*-vinyl-2-pyrrolidone (NVP) onto polyethylene films has been studied.^{1–5} Also, the modification of low-density polyethylene (LDPE)-*g*-polyvinyl pyrrolidone (PVP) with α,β -unsaturated nitriles¹ and dimer malonitrile⁶ has been reported to improve both the stability of the swelling of the membranes and the free movement of functional groups such as amidoxime groups, which are converted from cyano

groups containing the modified grafted membranes. The amidoxime groups have a more hydrophilic character than that of the nitrile function and play a vital role in the environmental monitoring of toxic metals. Thus, adsorbents containing $\text{H}_2\text{N}-\text{C}=\text{N}-\text{OH}$ groups have been studied for the recovery of uranyl ions from sea water.^{7–10} Furthermore, very few articles have been published for transition-metal uptake by poly(amidoxime) resins at various pHs.^{11–14} For example, suitable pHs for chelating copper ions are 4–6.^{11,12} Kabay and Egawa⁸ reported that the sorption capacities of copper and uranium were 3.6 and 1.47 mmol/g, respectively. The rate of sorption of copper-ion exchange was rapid (i.e., $t_{1/2} < 9$ min).¹¹

In this study, we examined the modification of LDPE-*g*-PVP with cinnamitrile derivatives, the preparation of amidoximated and grafted LDPE, and the use of hydrophilic amidoxime copolymers for chelating copper(II) in aqueous solutions through the adsorption of metal ions during the complexation process. The synthesis of heterocyclic compounds on the modified polymers was also studied. The graft copolymer-metal complex or isoxazole containing the modified graft copolymers was confirmed with infrared

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(IR) spectrophotometry, UV, elemental analysis (EA), energy-dispersive spectroscopy (EDS), electron spin resonance (ESR), and scanning electron microscopy (SEM). The thermal properties of the various modified films were examined with thermogravimetric analysis (TGA) to probe the stability of the bonds via the structure of the modified and grafted copolymers.

EXPERIMENTAL

Materials

LDPE films 70 mm thick (El-Nasr Co., Cairo, Egypt) were used as the base polymer. NVP (Merck, Hohenbrunn, Germany; 99% pure) was used without further purification. Cinnamitrile and benzylidene malononitrile (Aldrich, Milwaukee, WI) were used as received. Copper(II) nitrate [Cu(NO₃)₂] and other chemicals were reagent-grade and were used without further purification.

Graft polymerization

The graft copolymers were prepared by the direct radiation grafting method, in which strips of LDPE were immersed in an NVP/dimethylformamide solution in glass ampules. Ferric chloride (0.1 wt %) was added to the monomer and solvent to reduce the homopolymerization during radiation grafting. The glass ampule was sealed after deaeration with nitrogen gas for 5 min and then subjected to ⁶⁰Co γ rays at a dose rate of 0.83 Gy/S. The grafted films were removed and washed thoroughly with hot distilled water and were soaked overnight in water to extract the residual monomer and homopolymer. Finally, the grafted film was dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting was determined as the percentage increase in the weight as follows:

$$\text{Degree of grafting (\%)} = \frac{M_g - M_0}{M_0} \times 100$$

where M_g and M_0 are the weights of the grafted and initial films, respectively.

Preparation of the modified and grafted films with the cinnamitrile derivatives

A colorless grafted film (2 cm \times 3 cm) was immersed in a solution of cinnamitrile or benzylidene malononitrile (~5 g) and a few drops of triethylamine or piperidine in ethanol (100 mL). The reaction mixture was refluxed for 20 h. The faintly colored film was removed and washed with distilled water and ethanol, and this was followed by drying over filter paper.

Fourier transform infrared (FTIR) revealed the presence of cyano groups.

Preparation of the amidoxime films

The grafted LDPE modified with cinnamitrile or benzylidene malononitrile was reacted with a hydroxylamine hydrochloride solution (~3 g) in 100 mL of ethanol. The reaction mixture was refluxed and stirred for 2 h at 50°C. The films were dried, and the conversion to an amidoxime structure was determined by the disappearance of C \equiv N groups from the FTIR spectra.

Synthesis of the amidoxime copolymer-metal complexes

The amidoximated and grafted LDPE films were immersed in 1.0M NaOH in a water bath at 90°C for 15 min. The amidoxime sodium salt films that formed were reacted with 1.0 wt % Cu(NO₃)₂ at pH 6 for less than 9 min to form a dark brown, amidoximated, copper(II)-complexed film of grafted LDPE. The complexed film was characterized with different techniques, such as UV, EDS, and ESR.

Swelling measurements

The cleaned and dried LDPE-g-PVP films and the grafted LDPE-g-PVP films modified with cinnamitrile or benzylidene malononitrile were immersed in distilled water for 24 h. The films were removed, blotted with absorbent paper, and immediately weighed. The swelling percentage was calculated as follows:

$$\text{Swelling (\%)} = \frac{\text{Swollen weight} - \text{Dry weight}}{\text{Dry weight}} \times 100$$

IR spectra

IR spectra were taken for the grafted and modified LDPE films with a Shimadzu (Kyoto, Japan) 5000 FTIR spectrometer. The test films were used without diluents or supports.

Ultraviolet-visible (UV-vis) spectrophotometry

UV-vis spectrophotometry measurements were carried out over the wavelength range of 200–800 nm with a PerkinElmer $\lambda_{3\beta}$ instrument (Ueberlingen, Germany). The test films were mounted in a sample compartment as they were.

EDS

The EDS chemical area mapping of various metal-treated films was performed with a Link Exl II energy-dispersive spectrometer (Oxford Instruments Analytical, Hywycombe, Bucks, UK), attached to a scanning electron microscope to measure the absorbed ions from solution.

ESR

ESR measurements were carried out at room temperature with a Bruker model ECS 106 spectrometer in the X-band range (9.4 GHz) (Rheinstetten-Forchheim, Germany). The Landé factor (g) values were estimated with a Varian Standard Strong Pitch instrument ($g = 2.0028$). The copolymer films were cut into strips and placed in sample tubes. The stretching direction of the films was either parallel or perpendicular to the axis of the magnetic field.

SEM

The grafted, modified and grafted, and metal-treated, modified, and grafted LDPE films with Cu(II) ions at room temperature were examined with a JEOL (Akishima, Japan) JSM-6300 scanning electron microscope at 20 kV.

TGA

TGA was carried out in a dynamic atmosphere of pure nitrogen gas with a Shimadzu DSC 50 analyzer at a heating rate of 20°C/min and within a temperature range of 25–500°C.

RESULTS AND DISCUSSION

IR spectroscopy of the grafted and modified copolymers

Grafting LDPE with NVP (LDPE-*g*-PVP) added chemical reactivity to the polymeric chain. Thus, LDPE-*g*-PVP had two active sites. The first one, a carbonyl group that showed no chemical reactivity toward nucleophilic reagents, may have been due to a steric effect, lower reactivity of the amide carbonyl, or both.^{1,6} This result prompted us to investigate the chemical reactivity of the α -methylene group.

Figure 1 shows the IR spectra of grafted LDPE with NVP, grafted LDPE modified with cinnamitrile, and grafted LDPE modified with benzylidene malonitrile. LDPE-*g*-PVP had sharp absorption bands at 3434 and 1658 cm^{-1} that were characteristic of the structure of NVP at a grafting yield of 43 wt %. Thus, both cinnamitrile **1a** and benzylidene malonitrile **1b** reacted with LDPE-*g*-PVP to undergo a Michael addition reaction to afford modified polymers **2a** and

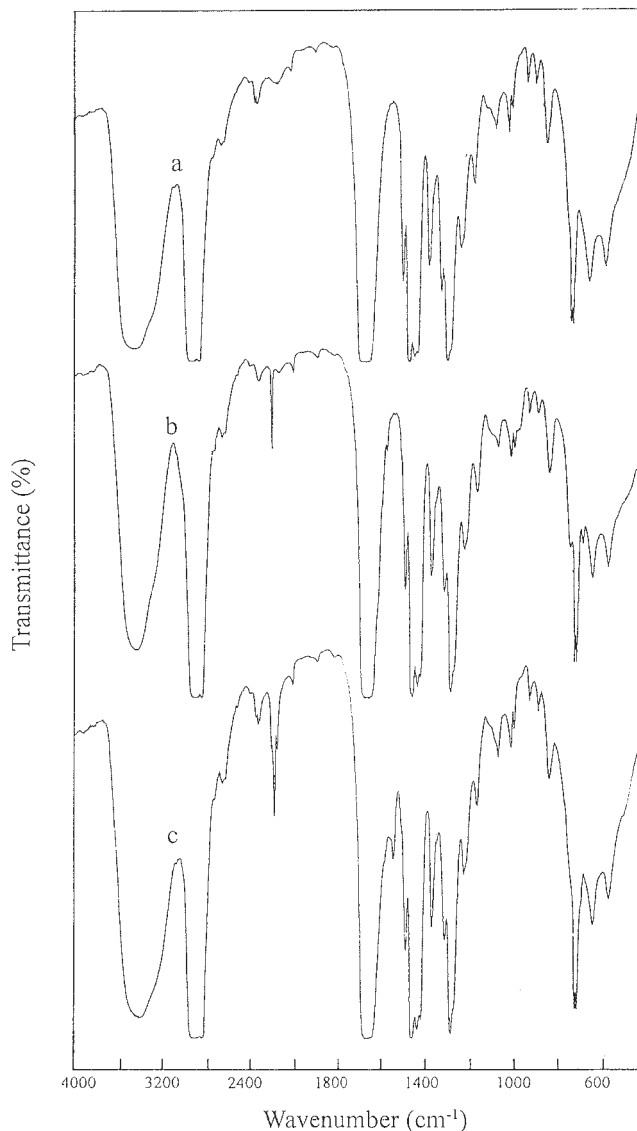
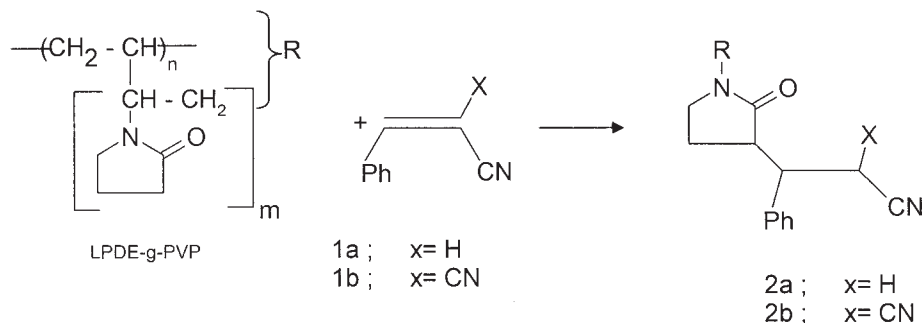


Figure 1 IR spectra of (a) LDPE-*g*-PVP, (b) LDPE-*g*-PVP modified with cinnamitrile, and (c) LDPE-*g*-PVP modified with benzylidene malonitrile, all with 43% grafting.

2b, respectively (Scheme 1). The reaction product was established with IR spectra, which revealed the presence of a cyano group at 2215 cm^{-1} with respect to compound **2a** and at 2164 and 2191 cm^{-1} with respect to compound **2b**, as shown in Figure 1.

Figure 2 shows the IR spectra of grafted LDPE modified with cinnamitrile and amidoximated and grafted LDPE with the same grafting yield (52 wt %). LDPE-*g*-PVP modified with cinnamitrile had a new characteristic sharp absorption at 2216 cm^{-1} due to $\text{C}\equiv\text{N}$ groups. These nitrile groups completely disappeared, whereas the $\text{C}\equiv\text{N}$ groups were converted into amidoxime groups, during amidoximation. As a result of amidoximation, the absorption band appearing at 3434–3200 cm^{-1} characterized the hydroxyl and amine groups in the $\text{H}_2\text{N}-\text{C}=\text{N}-\text{OH}$ groups.



Scheme 1

Swelling behavior

Figure 3 shows the water uptake as a function of the degree of grafting for LDPE-g-PVP, grafted LDPE modified with cinnamitrile, and grafted LDPE modified with benzylidene malonitrile. The swelling of the grafted film, the grafted film modified with cinnamitrile, and the grafted film modified with benzylidene malonitrile increased significantly with the degree of grafting. However, the water uptake of the grafted film modified with cinnamitrile was higher than that of the nonmodified grafted polymer and the grafted polymer modified with benzylidene malonitrile. This may have been due to an increase in the surface area of the modified grafted film, the formation of hydrogen bonding with the nitrile groups, and lower steric hindrance in comparison with that of the grafted film containing benzylidene malonitrile.

The results suggested that the improvement in the swelling behavior with modification by cinnamitrile was higher than that of the grafted film and the grafted film modified with benzylidene malonitrile

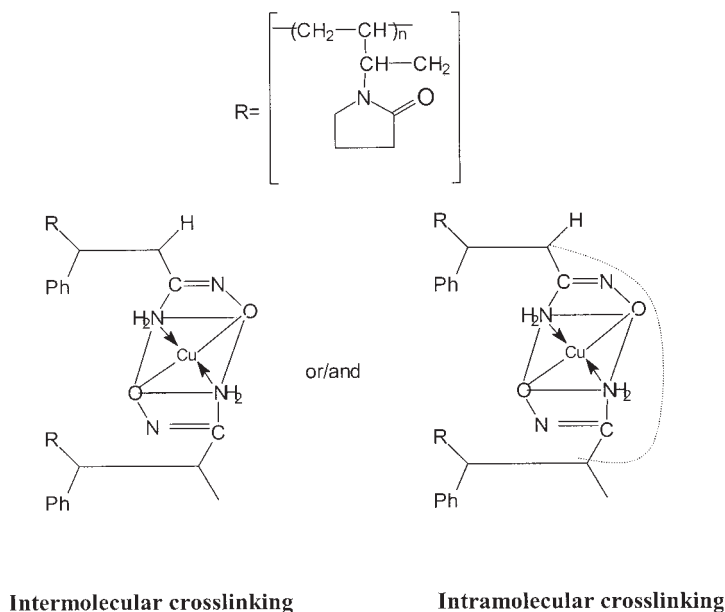
because of the high steric effect of the two nitrile groups in its structure.

Complex formation

The preparation of the complex of amidoximated cinnamitrile in LDPE-g-PVP with copper(II) ions was confirmed by spectrophotometry.

EDS and UV-vis measurements

Figure 4 shows EDS of a Cu(II) solution. The amidoximated cinnamitrile through LDPE-g-PVP greatly absorbed Cu(II) ions (88.43%) from the solution at pH 6. The UV-vis measurements showed that the peak of the Cu(NO₃)₂ solution appeared at 820 nm. However, the broad peak of the copper(II) complex of amidoximated cinnamitrile via the grafted film appeared at 646.6 nm, and this may have been due to the square-planar environment. It represents a stable structure of five-membered rings of a complex.¹⁴ The proposed structure is as follows:



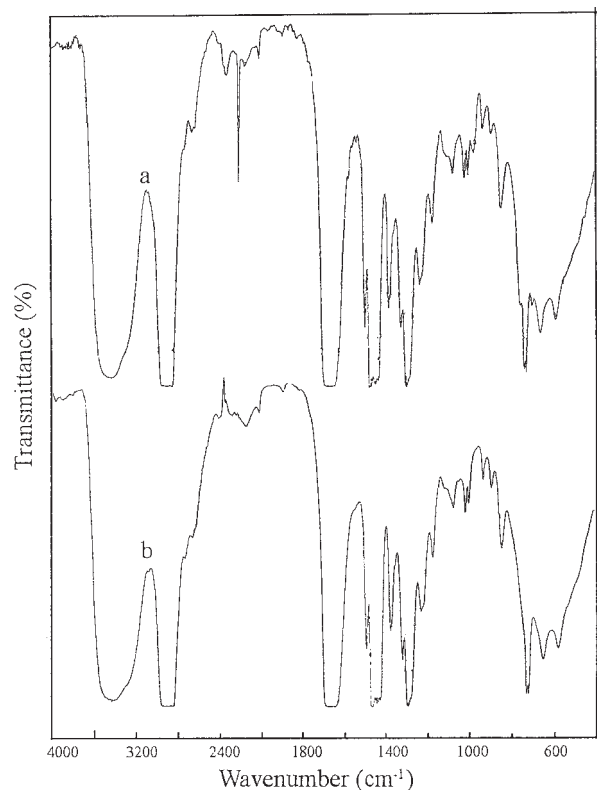


Figure 2 IR spectra of (a) grafted LDPE modified with cinnamitrile and (b) amidoximated and grafted LDPE modified with cinnamitrile, both with 52 wt % grafting.

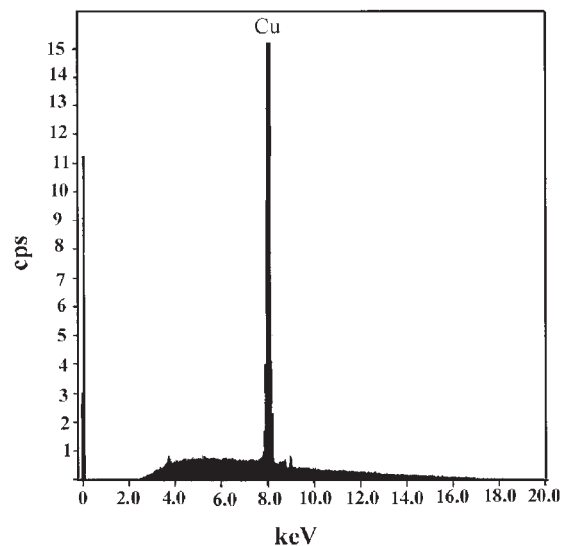


Figure 4 EDS for amidoximated LDPE-g-PVP complexed with Cu(II) ions.

ESR investigation

The X-band ESR spectrum of the polycrystalline sample of amidoximated cinnamitrile/LDPE-g-PVP with Cu(II) at room temperature was axial with parallel Landé factor (g_{\parallel}) = 2.16 and perpendicular Landé factor (g_{\perp}) = 2.09; this was consistent with a $d_{x^2-y^2}$ ground state for the compound. The average value of g [$\langle g \rangle = \frac{1}{3}(2g_{\perp} + g_{\parallel}) = 2.11$] and the low value of g_{\parallel} (<2.30) indicated the covalent-bond char-

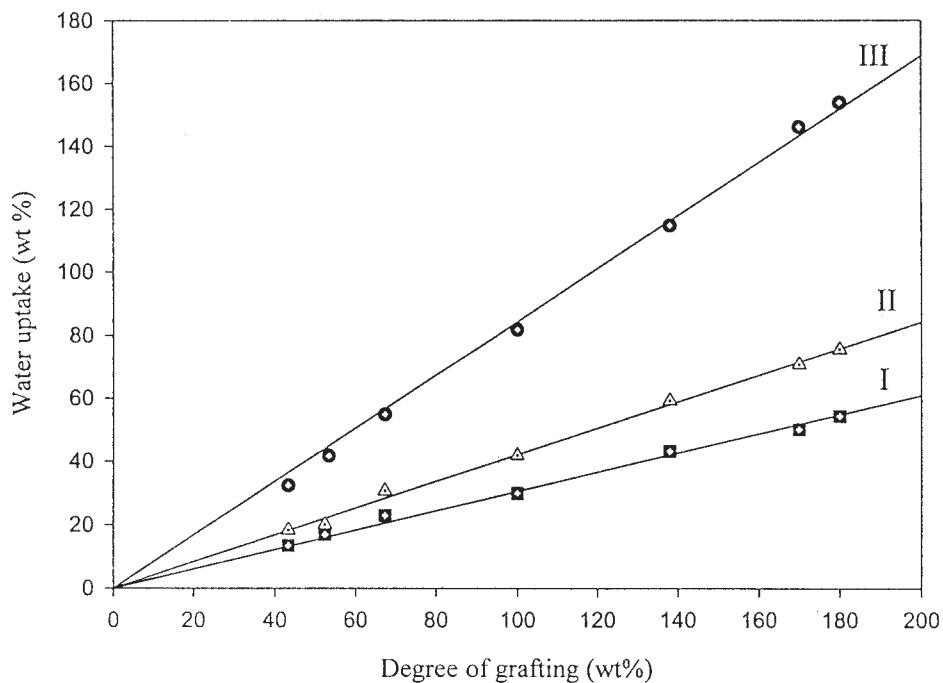
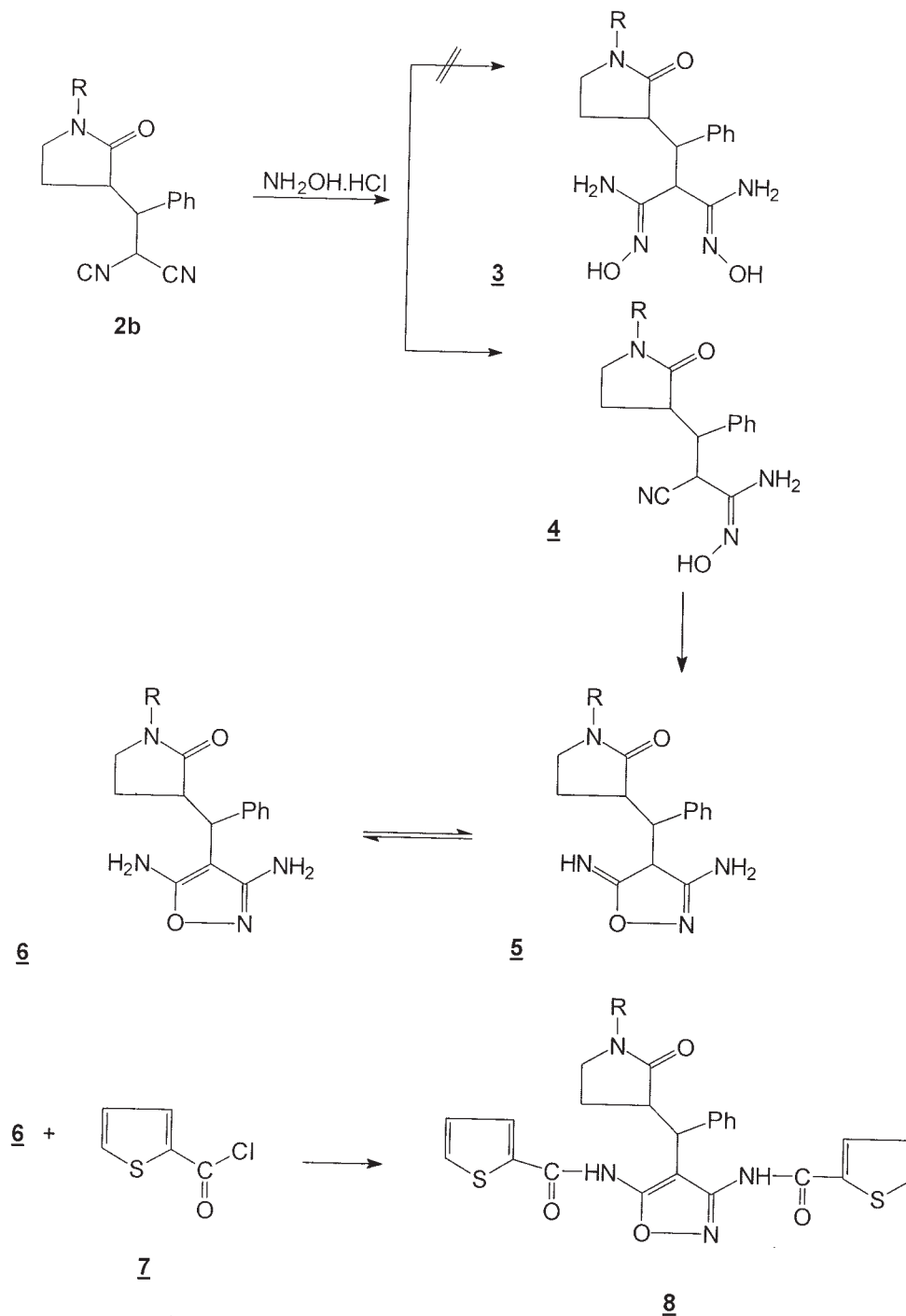


Figure 3 Water uptake versus the degree of grafting for (■) LDPE-g-PVP, (△) LDPE-g-PVP with benzylidene malonitrile, and (●) LDPE-g-PVP with cinnamitrile.



Scheme 2

acter between the Cu-amidoximated cinnamionitrile and LDPE-g-PVP. G is the extent of the dipolar-dipolar interaction in the solid state $[(g_{\parallel} - 2)/(g_{\perp} - 2) = 1.8]$ and can be taken as evidence for the strong Cu-Cu interaction expected in such compounds between the adjacent Cu(II) ions in the solid state.

The spectrum showed a broad signal in the half-field region (1586G) of $g = 4.39$, which was characteristic of

the forbidden selection rule for the electronic spin change in the ESR ($\Delta M_s = \pm 2$) transitions characteristic of the polymeric nature of this complex. The dipolar-dipolar interaction was further supported by the large line width of the signals. The lack of a hyperfine structure in the spectrum suggested that the intermolecular exchange interactions were operative,¹⁵ but these interactions were not strong enough to combat the dipolar interaction.¹⁶

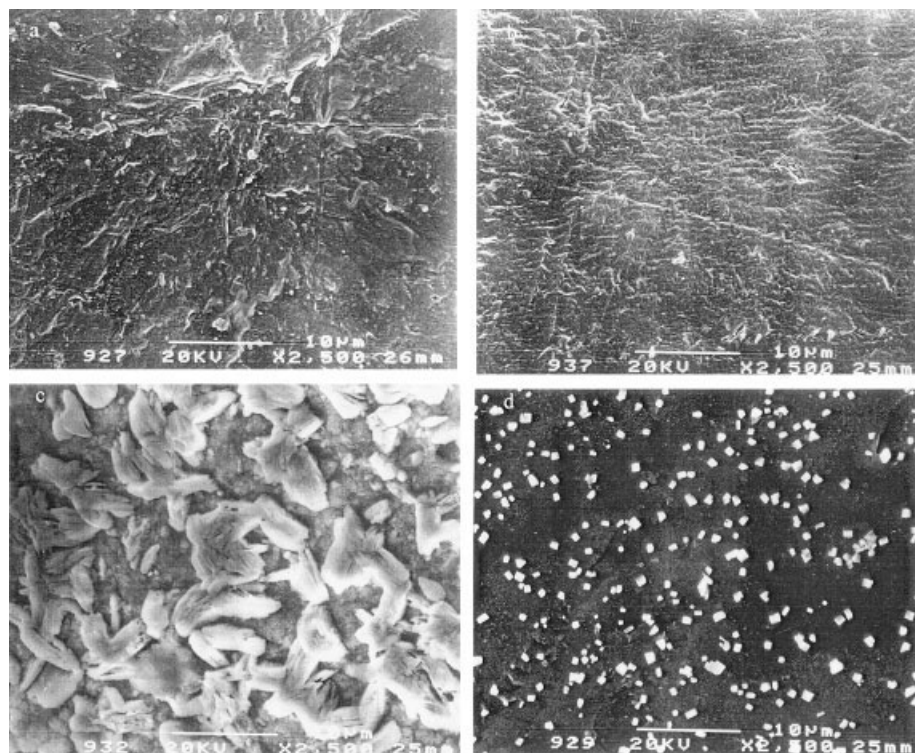


Figure 5 SEM micrographs of (a) LDPE-g-PVP, (b) LDPE-g-PVP/AO, (c) LDPE-g-PVP/AO/Cu, and (d) LDPE-g-PVP/isoxazole at room temperature.

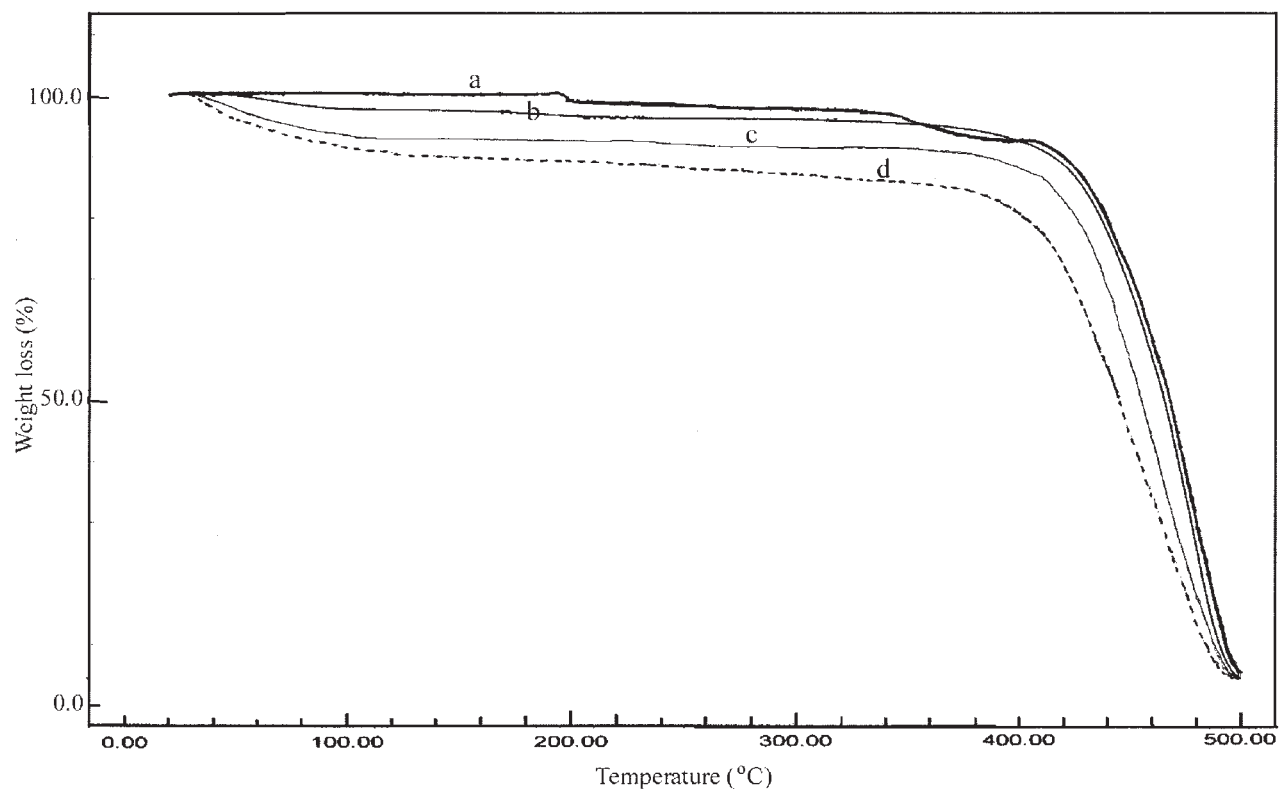


Figure 6 TGA curves for (a) LDPE-g-PVP, (b) LDPE-g-PVP/AO, (c) LDPE-g-PVP/isoxazole, and (d) amidoximated and grafted LDPE complexed with Cu(II) ions.

TABLE I
TGA

Sample	25–100 (°C)	100–200 (°C)	200–300 (°C)	300–400 (°C)	400–500 (°C)	Total weight loss (%)
LDPE-g-PVP	—	—	1.941	4.824	92.678	99.813
LDPE-g-PVP/AO	2.498	1.237	1.056	3.739	88.338	96.508
LDPE-g-PVP/isoxazole	7.135	0.516	0.735	3.578	84.444	96.408
LDPE-g-PVP/AO/Cu	5.131	2.139	1.742	5.157	70.647	84.816

Preparation of isoxazole

When we aimed to prepare diamidoxime derivative **3** from **2b** with hydroxylamine hydrochloride cyclization, the formation of isoxazole derivative **6** took place. **6** was believed to be formed via the addition of one molecule of hydroxylamine hydrochloride to give intermediate **4**. The latter was readily cyclized, and the reaction conditions led to nonisolated intermediate **5**. This intermediate was tautomerized to give the final isolated product (**6**). The reaction product was established from spectral data. Thus, IR revealed the presence of characteristic bands for the isoxazole ring, such as the $\nu_{C=N}$ ring at 1557 cm^{-1} , the $\nu_{C=C}$ ring at 1429 cm^{-1} , and ν_{ring} at 1366 , 916 , and 845 cm^{-1} ,¹⁷ in addition to a broad band at 3398 cm^{-1} for the amino groups. Moreover, the UV spectrum showed characteristic bands for the 2,5-diamino derivatives at 235 and 267 nm.¹⁸ Furthermore, the chemical elucidation of the reaction product was performed; compound **6** reacted readily with 2-thiophenecarbonyl chloride (**7**) to yield diamide derivative **8**. This reaction product was established from the elemental analysis, which revealed the presence of 18.34% sulfur, and IR showed the amide carbonyl at 1658 cm^{-1} . The reactions are shown in Scheme 2.

Structural and morphological investigation

Figure 5 shows the morphologies of LDPE-g-PVP, amidoximated LDPE-g-PVP modified with cinnamitrile, modified and grafted LDPE-g-PVP complexed with Cu(II), and LDPE-g-PVP/isoxazole recorded at room temperature. Figure 5(a) shows some crystallinity, which was due to the embedding of PVP chains in the matrix of LDPE. Furthermore, the modification of the grafted film with cinnamitrile and its amidoximation increased the amorphous structure and led to a rough surface morphology, as shown Figure 5(b). However, the SEM micrograph of amidoximated and grafted LDPE complexed with Cu(II) showed a crystalline gathering structure because of the formation of the copper(II) complex. Meanwhile, the formation of isoxazole during the amidoximation of benzylidene malonitrile via LDPE-g-PVP ap-

peared to be from regular gatherings similar to groups of stars at night.

The results suggested that the change in the surface morphology may have been due to the addition of metal ions and may have formed a square-planar environment as a geometrical structure of the Cu(II) complex. Also, the formation of a new ring such as isoxazole, which is depicted in Figure 5(d), may have affected the surface morphology of the copolymer films.

TGA

Figure 6 illustrates TGA curves for LDPE-g-PVP, amidoximated and grafted LDPE modified with cinnamitrile, LDPE-g-PVP modified with benzylidene malonitrile to give isoxazole, and LDPE-g-PVP/AO/Cu complex. Table I and Figure 6 show that the weight loss (%) of the initial decomposition temperature within 25–200°C for the grafted, amidoximated, isoxazole, and complexed films due to the removal of water and hydrogen bonding in the polymeric material during the initial heating. The nonmodified film was more stable than the modified and grafted films at 25–300°C. Afterwards, the weight loss increased for the grafted and modified films, whereas it decreased in the complexed film because of the presence of Cu(II) ions through the structure at 200–400°C. Moreover, the stability of the complexed polymer vanished because of the complete decomposition of its geometrical structure. Therefore, the stability sequence of various polymeric materials was as follows: LDPE-g-PVP/AO/Cu > AO \geq isoxazole > LDPE-g-PVP (glass-transition temperature: $107.66^\circ\text{C} < 108.53^\circ\text{C} \leq 109.73^\circ\text{C} < 111.03^\circ\text{C}$). The results indicated that with an increase in the glass-transition temperature of the polymeric compounds, the stability decreased.

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