Preparation and Radiation Effect on Composite Films Containing Both Polypropylene and Novel Phthalocyanines with Functionalized Bulky Phenoxy Groups

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ABSTRACT: Novel symmetrically substituted 2,3,9,10,16, 17,23,24-octa(p-methylphenoxy)phthalocyanines [(p-methyl-phenoxy)$_8$PcM (**3–5**, where Pc is phthalocyanine and M is H$_2$ or one of its metal complexes, Mg or Zn, respectively)] were synthesized and characterized as target precursors for the preparation of polypropylene (PP)/Pc composite films [PP/(p-methylphenoxy)$_8$PcM (labeled **I–III** for composites with Pcs **3–5**, respectively)]. We prepared the composites by embedding the Pcs into the PP using the cast method. The effects of γ irradiation on the physicochemical properties of PP after the formation of the PP/(p-methylphenoxy)$_8$PcM composite films (**I–III**) were studied. The structure of the prepared composite series (**I–III**) was characterized with Fourier transform infrared spectroscopy. For composite **III**, minor differences in the Fourier transform infrared spectra were observed after irradiation treatment; these occurred because the zinc Pc additives in the repeating units of composite **III** acted as stabilizing elements against γ-irradiation-induced degradation because of the delocalization of excitation energy in the double and aromatic units and also because of the large ionic radius of Zn in composite **III** compared with those in composite **II** (containing Mg) and composite **I** (metal-free). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 134–141, 2011

Key words: radiation; synthesis; UV-vis spectroscopy

INTRODUCTION

Polymer composites containing phthalocyanines (Pcs) represent a new type of materials, both in Pc-based materials and in the field of composite materials. According to this, two groups of modified polymer matrices containing physically attached and chemically bound Pcs can be distinguished.[1] Polymer composite films with incorporated Pcs have attracted much attention in the fields of catalysis, biomaterials, nonlinear optics, sensors, and so on[2–4] because of their high thermostable and photostable properties and low combustibility.[5–8]

The evolution of polymer composite technology is allowing the creation of new composite polymeric materials made from synthetic Pcs supported on a polymer matrix; these are attractive objects for investigation in this area of science materials.[5–8]

Pcs and metallophthalocyanines, one of the best known conjugated disklike molecules, have attracted special interest for use as commercial dyes and coloring agents in many application fields[9–16] because of their thermal and chemical stabilities.

Polypropylene (PP) is widely used in medical and pharmaceutical products and in the packaging industry. Products made of PP for the medical industry (e.g., syringes, catheters) generally require sterilization before use. Typical sterilization doses are between 25 and 40 kGy.[17] Both γ and electron-beam irradiation are used for sterilization purposes.

The radiation sterilization of food-packaging materials and medicinal and healthcare products and the radiation pasteurization of foods are among the most significant practical applications of ionizing radiation.[18] In the medical device industry, ionizing irradiation (mainly, γ radiation) is the second most important cold sterilization method behind ethylene oxide sterilization.[19,20]

Both electron-beam radiation and γ radiation may be used for sterilization purposes.[21] γ irradiation is used because of its higher penetrating capability and negligible heat production.[17,21] The recognized average dose for sterilization is 25 kGy or 2.5 Mrad.[17]

The major chemical changes occurring in polymers as a result of ionizing irradiation are (1) the scission and/or crosslinking of the polymeric chains, with the net effect determining the changes in the polymer properties; (2) the formation of gases and low-molecular-weight radiolysis products; and (3) the

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formation of unsaturated bonds.[22,23] Also, discoloration is a major problem in the radiation sterilization of disposable plastic items for medical use (e.g., syringes, vials, tubing).[24,25] The net effect depends on the particular material,[17,18] radiation dose,[22,23] irradiation temperature,[26,27] irradiation atmosphere (with oxygen or *in vacuo*), dose rate, and additives used.[28–31] For irradiation in the presence of air, oxygen reacts with the free radicals produced by irradiation, and the peroxide radicals formed can then undergo further reactions that lead to chain scission and the formation of hydroperoxides, carbonyl compounds, acids, discoloration, crosslinking, and so on.[30,32,33]

Montforts et al.[1] reported the synthesis, properties, and characterization of novel symmetrically substituted 2,3,9,10,16,17,23,24-octa(*p*-methylphenoxy)phthalocyanines [(*p*-methylphenoxy)$_8$PcM (**3–5**, where M is H$_2$, Mg, or Zn, respectively)], which were prepared by the high-temperature cyclotetramerization processes of their corresponding phthalonitriles [4,5-bis(*p*-methylphenoxy)phthalonitrile (**2**)]. The aim of this study was to use the prepared Pcs (**3–5**) as target precursors for the preparation of PP/(*p*-methylphenoxy)$_8$PcM composite films (labeled **I–III** for composites with Pcs **3–5**, respectively) by the embedding of the synthetic Pcs into PP with the cast method.

The introduction of phenoxy functional groups to the periphery of the Pc skeleton increases the distance between the electron-conjugated systems of the Pcs and may enhance the solubility of these compounds. This has been demonstrated by the attachment of branched, aliphatic, and polar side chains to the Pc skeleton.[34–41]

In our previous study,[42] we examined the effect of γ irradiation in the presence of air on the thermal and chemical properties of polystyrene through the addition of iron phthalocyanine [(OR)$_8$PcFe(Pyz)$_2$] to afford polystyrene/(OR)$_8$PcFe(Pyz)$_2$ composites at low integral doses (0–60 kGy) of γ radiation.

The objective of this study was to extend to our previous work by studying the effect of γ irradiation (0–100 kGy) in the presence of air at room temperature on the chemical properties of novel symmetrically and asymmetrically metal-free metallophthalocyanines carrying long-chain alkoxy groups or axial ligands, which we reported previously.[43–45]

EXPERIMENTAL

Generally, all manipulations for the synthesis of the Pcs were performed under nitrogen with the standard Schlenk technique unless otherwise specified.

Materials

4,5-Dichlorophthalonitrile (**1**) and 4-methylphenol (Aldrich, Germany) were commercially available and were used as purchased. All other reagents, solvents, and metal salts were reagent-grade quality, were obtained from commercial suppliers, and were used as received.

The polymeric matrix used was PP, was commercially available, and was used as purchased without any additives or pigments.

Physical measurements

^{1}H-NMR spectra were measured on a Bruker ARX 250 (250.133-MHz) NMR spectrometer (Bruker Daltonik GmbH, Bremen, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Mattson 1000 FTIR spectrophotometer (Unicam, Ltd., England) by the preparation of pellets with KBr. The ultraviolet–visible (UV–vis) spectra were taken in dichloromethane with a PerkinElmer Lambda 2 spectrometer. Field desorption mass spectra measurements were carried out on a Varian MAT 711 A spectrometer and are reported in mass/charge (m/z). Elementary analyses were performed on a Carlo Erba elemental analyzer 1104, 1106.

Synthesis of (*p*-methylphenoxy)$_8$PcM (3–5)

2

To a suspension of **1** (1 g, 5 mmol) and potassium carbonate (4.00 g) in dimethyl sulfoxide (15 mL), 4-methylphenol (1.6 g, 15 mmol) was added. The mixture was heated to 90°C under N$_2$ for 30 min; this was followed by the addition of another portion of potassium carbonate (3.00 g). The reaction mixture was stirred at 90°C for an additional 4 h, then cooled to room temperature, and poured into water (100 mL). The water phase was extracted with CH$_2$Cl$_2$. The combined organic phases were dried with MgSO$_4$. After the removal of the solvent under reduced pressure, the residue was purified with column chromatography (SiO$_2$) with CH$_2$Cl$_2$ as an eluent; this afforded **2** as a pale green viscous oil. This oily compound was dried under high vacuum, during which it solidified (mp = 90–95°C).

IR (KBr, ν, cm^{-1}): 3442, 2933, 2221 (─CN); 1577, 1511, 1302, 1233. ^{1}H-NMR (250 MHz, CD$_2$Cl$_2$, δ, ppm): 7.30 (s, 2 H), 7.20 (d, 4 H), 6.96 (d, 4 H), 0.92 (s, 6 H). Mass spectrometry (electron impact): m/z (%) = 340.40 (70) [M$^+$]: 340.38. ANAL. Calcd for C$_{22}$H$_{16}$N$_2$O$_2$ (340.38): C, 77.63%; H, 4.74%; N, 8.23%. Found: C, 76.51%; H, 5.30%; N, 7.19%.

3

A mixture of **2** (1.4 g, 4 mmol) and 1,8-diazabicyclo-5,4-undec-7-ene (1.5 mL) in 1-pentanol (25 mL) was refluxed at 150°C for 22 h under N$_2$. After cooling, the mixture was poured into CH$_3$OH (50 mL). The

suspended solution was centrifuged, and the green precipitate was filtered, washed with CH_3OH, and dried at 60°C. The crude product was subjected to column chromatography (SiO_2), and we eluted it with 3 : 1 CH_2Cl_2/n-hexane. After the removal of the solvent under reduced pressure and 10 h of drying at 60°C in $vacuo$, the reaction yielded 0.94 g (69%) of 3.

IR (KBr, ν, cm^{-1}): 3430 (br); 2935, 1609, 1510, 1444, 1382, 1279, 1222, 1168, 1079, 1019, 879, 758. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): −2.1 to −1.8 (br, 2H, NH), 8.40 (s, 8 H), 7.10–7.20 (m, 32 H), 1.23 (s, 24 H). UV–vis ($CHCl_3$, λ_{max}, nm): 697, 662, 640, 599, 340. Mass spectrometry (field desorption): $m/z = 1363.54$ (66) [M^+]. Anal. Calcd for $C_{88}H_{66}N_8O_8$ (1363.54): C, 77.52%; H, 4.88%; N, 8.22%. Found: C, 76.68%; H, 5.17%; N, 9.12%.

4

Magnesium turnings (80 mg) were suspended in about 10 mL of 1-pentanol. This suspension was heated to 150°C (reflux) and maintained at that temperature until an amalgam was formed (∼ 1 h). 1-Pentanol (20 mL) was added to this amalgam, followed by 2 (1.4 g, 4 mmol). The suspension was heated to 150°C and stirred for 24 h. After cooling, the mixture was poured into 150 mL of a mixture methanol and water (5/1). The formed precipitate was isolated by centrifugation and washed several times with methanol. The crude product was subjected to column chromatography (SiO_2) and elution with 3 : 1 CH_2Cl_2/n-hexane. After removal of the solvent under reduced pressure and 10 h of drying at 60°C in $vacuo$, the reaction yielded 4 as a green solid (1.08 g, 76%).

IR (KBr, ν, cm^{-1}): 2938, 1610, 1513, 1448, 1392, 1270, 1221, 1170, 1082, 1017, 878, 750. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 8.33 (s, 8 H), 7.06–7.16 (m, 32 H), 1.28 (s, 24 H). UV–vis ($CHCl_3$, λ_{max}, nm): 688, 618, 357. Mass spectrometry (field desorption): $m/z = 1385.83$ (58) [M^+]. Anal. Calcd for $C_{88}H_{64}N_8O_8Mg$ (1385.83): C, 76.27%; H, 4.65%; N, 8.09%. Found: C, 75.68%; H, 5.47%; N, 7.82%.

5

A mixture of 2 (1.4 g, 4 mmol), anhydrous zinc acetate (0.071 g, 0.39 mmol), and 1,8-diazabicyclo-5,4-undec-7-ene (1.5 mL) in 1-pentanol (25 mL) was refluxed at 155°C for 24 h under N_2. After cooling, the mixture was poured into 150 mL of a mixture of methanol and water (3/1). The formed dark green precipitate was isolated by centrifugation and washed several times with methanol. The crude product was subjected to column chromatography (SiO_2) and elution with 3 : 1 CH_2Cl_2/n-hexane. After
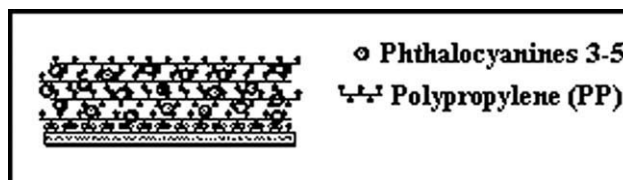
Figure 1 Formation of the composite films **I–III**.

the removal of the solvent under reduced pressure and 10 h of drying at 60°C in $vacuo$, the reaction yielded 1.13 g (79%) of 5.

IR (KBr, ν, cm^{-1}): 2939, 1611, 1508, 1440, 1392, 1285, 1213, 1159, 1084, 1016, 877, 753. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm): 8.48 (s, 8 H), 7.08–7.19 (m, 32 H), 1.28 (s, 24 H). UV–vis ($CHCl_3$, λ_{max}, nm): 678, 609, 353. Mass spectrometry (field desorption): $m/z = 1426.90$ [M^+]. Anal. Calcd for $C_{88}H_{64}N_8O_8Zn$ (1426.90): C, 74.07%; H, 4.52%; N, 7.85%. Found: C, 75.68%; H, 5.22%; N, 8.12%.

Preparation of the PP/(p-methylphenoxy)$_8$PcM composite films (I–III)

Pcs with concentrations of 1.5 wt % were mixed with PP in xylene at 60°C for 10 min and then cast onto a Petri dish with a diameter of 15 cm; they were then left to dry in an oven at 80°C for 4 h. The composite obtained with metal Pcs at a concentration of 1.5 wt % were composite **I** [PP/(p-methylphenoxy)$_8$PcH$_2$], composite **II** [PP/(p-methylphenoxy)$_8$PcMg], and composite **III** [PP/(p-methylphenoxy)$_8$PcZn; see Fig. 1].

Irradiation of the PP/(p-methylphenoxy)$_8$PcM composite films (I–III)

The prepared composites (**I–III**) were cut into small films with dimensions of 1×1 cm^2 and subjected to ^{60}CO γ rays with doses ranging from 20 to 100 kGy at a dose rate of 1.27 Gy/s.

RESULTS AND DISCUSSION

Synthesis and characterization of (p-methylphenoxy)$_8$PcM (3–5)

Synthesis of (p-methylphenoxy)$_8$PcM (3–5)

The synthetic route for the target Pcs **3–5** is given in Scheme 1. The starting material **2** was synthesized from commercially available **1** in good yield (70–80%).

The metal-free octa(p-methylphenoxy)phthalocyanine **3** was prepared via the cyclotetramerization reaction of the corresponding phthalonitrile **2** in 1-pentanol.

The metal-containing Pcs **4** and **5** were prepared readily by the metal-ion-mediated cyclotetramerization
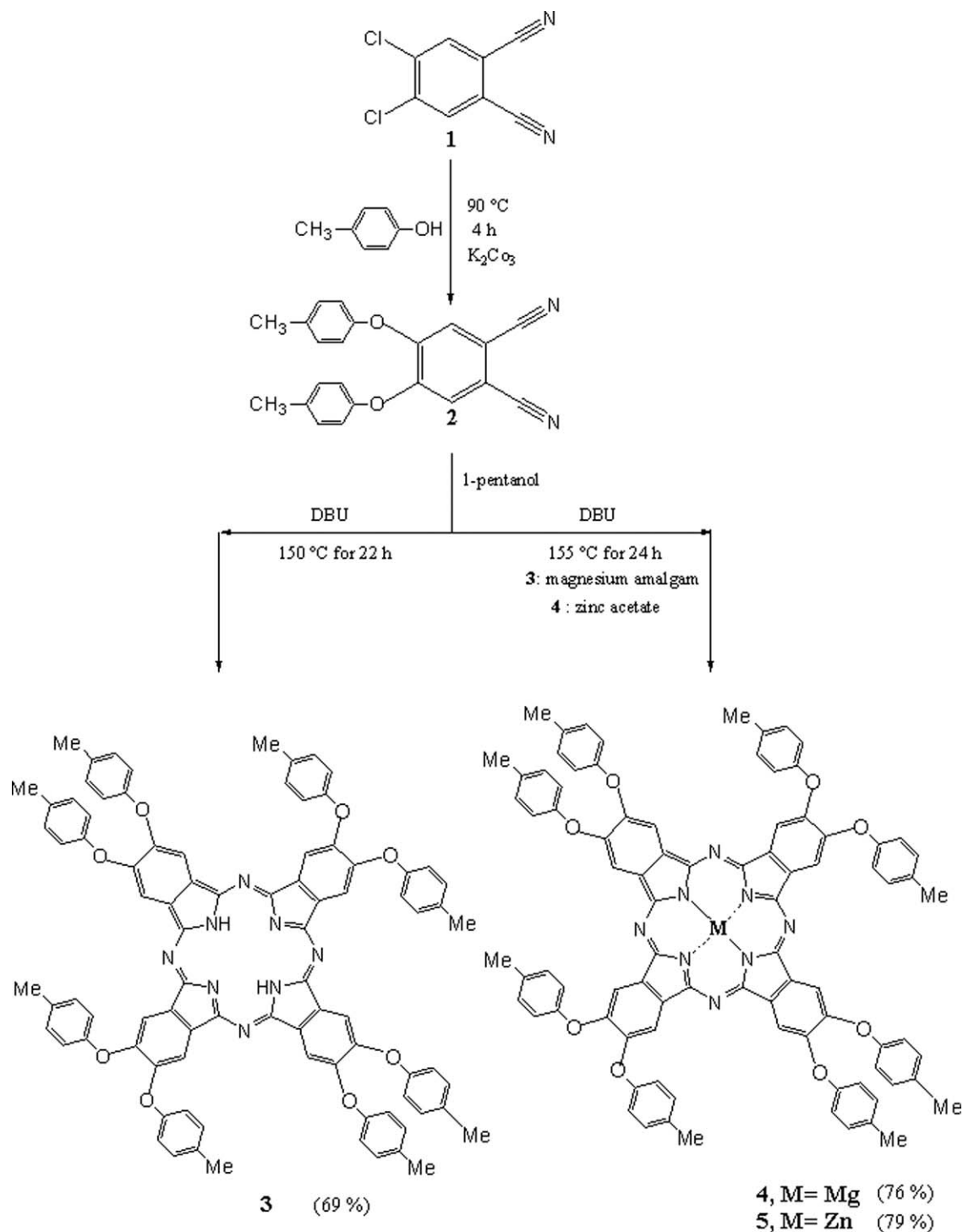
Scheme 1 Synthetic route for the target Pcs (**3–5**).

reaction of corresponding phthalonitrile **2** in 1-pentanol with the magnesium amalgam or anhydrous zinc acetate.

Column chromatography was used with 3 : 1 CH_2Cl_2/n-hexane as an eluent to obtain the appropriate Pcs in good isolated yield (76–79%) from the reaction mixtures. The intense green complexes **3–5** were highly soluble in most organic solvents, including chloroform and dichloromethane, at room temperature.

The structure and purities of Pcs **3–5** were confirmed by ^{1}H-NMR spectroscopy, elemental analysis, and UV–vis absorption spectroscopy.

The ^{1}H-NMR spectrum of **3** in CDCl$_3$ showed inner core NH protons of the metal-free octa(p-methylphenoxy)phthalocyanine **3**. The signals related to aromatic and aliphatic protons in the macrocyclic moieties and Pc skeleton gave significant absorbance characteristic of the proposed structure for Pcs **3–5**.
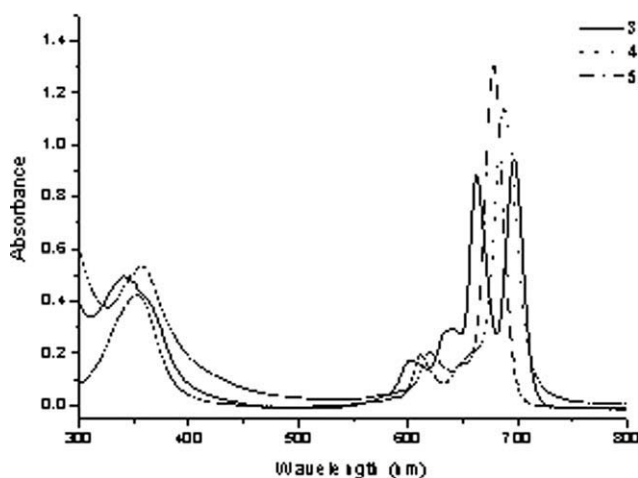
Figure 2   UV–vis spectra of **3** in CHCl$_3$, **4,** and **5**.

The aromatic protons appeared as a singlet at $\delta \approx$ 8.40 ppm, and the aliphatic methyl protons appeared as a singlet at $\delta \approx$ 1.3 ppm. The conformation of the presence of phenoxy groups in the derived Pcs **3–5** was clearly shown by the ^{1}H-NMR spectrum at $\delta =$ 7.10–7.20 ppm, which appeared as a multiplet.

The NH proton of metal-free Pc was also identified in the ^{1}H-NMR spectrum with a broad peak at $\delta = -2.21$ ppm, and the signal disappeared by deuterium exchange.

The IR spectra of the metal-free **3** and metallophthalocyanines **4** and **5** were very similar. The only difference was the presence of an NH stretching band at 3350–3440 cm^{-1} in the metal-free Pc **3** due to the inner core. This band was absent in the spectra of the metal complexes **4** and **5**.

Characterization of (*p*-methylphenoxy)$_8$PcM (**3–5**): UV–vis electronic absorption spectral studies

Electronic spectra are especially fruitful for establishing the structure of the Pcs. The Pcs exhibited typical electronic spectra with two strong absorption regions; one of them was in the UV region at about 300–350 nm (B band), and the other one was in the visible region at 600–700 nm (Q band).

The UV–vis spectrum of the metal-free octa(*p*-methylphenoxy)phthalocyanine **3** showed a doublet Q band at $\lambda_{max} = 697$ and 662 nm as a result of the D$_2$h symmetry, whereas the B band remained at 340 nm (Fig. 1).

The UV–vis spectra of metallophthalocyanines **4** and **5** in chloroform displayed intense Q bands around 678–688 nm with relatively sharp absorption peaks and almost no shoulder on the higher energy side, which would have corresponded to aggregated species and the B bands in the near UV region, around 350–357 nm. The magnesium(II) Pc **4** exhib-

ited an intense Q band around $\lambda_{max} = 688$ nm, and the Q band of the zinc(II) Pc **5** appeared at $\lambda_{max} = 678$ nm. These compounds showed the expected absorptions at the main peaks of the Q and B bands (see the Experimental section).

In the mass spectrum of prepared compounds **3–5,** the observed molecular ion peaks confirmed the proposed structure.

Spectroscopic characterization of the prepared composite films I–III: FTIR analysis

The FTIR spectra of the nonirradiated and irradiated (by γ irradiation) samples at different doses are shown in Figures 3–5. The FTIR spectra were practically identical; this indicated that any changes observed in the molecular structure were a result of irradiation.
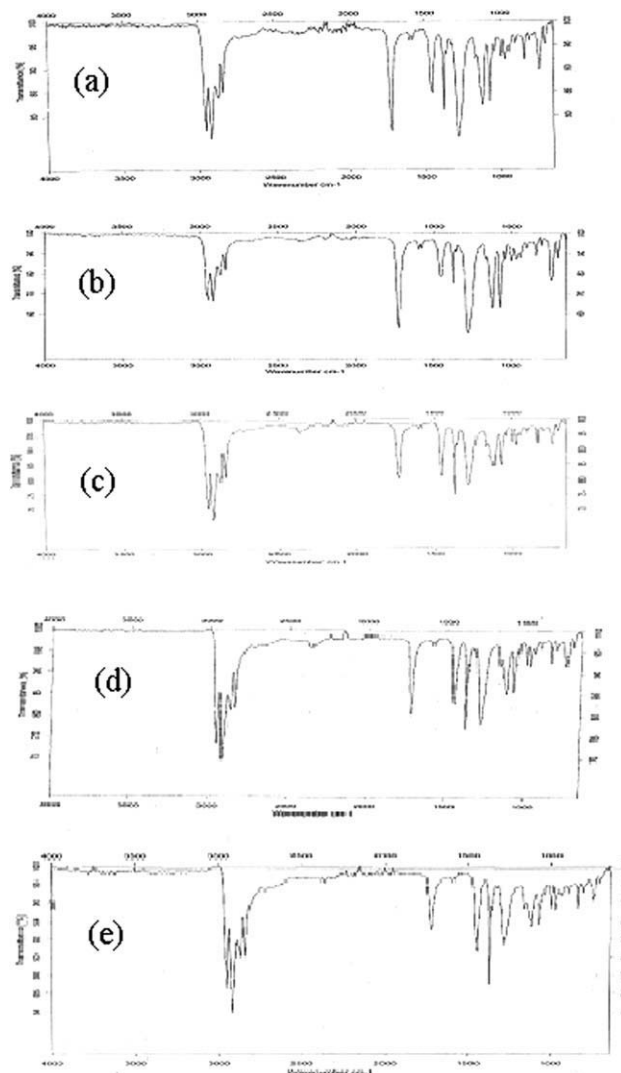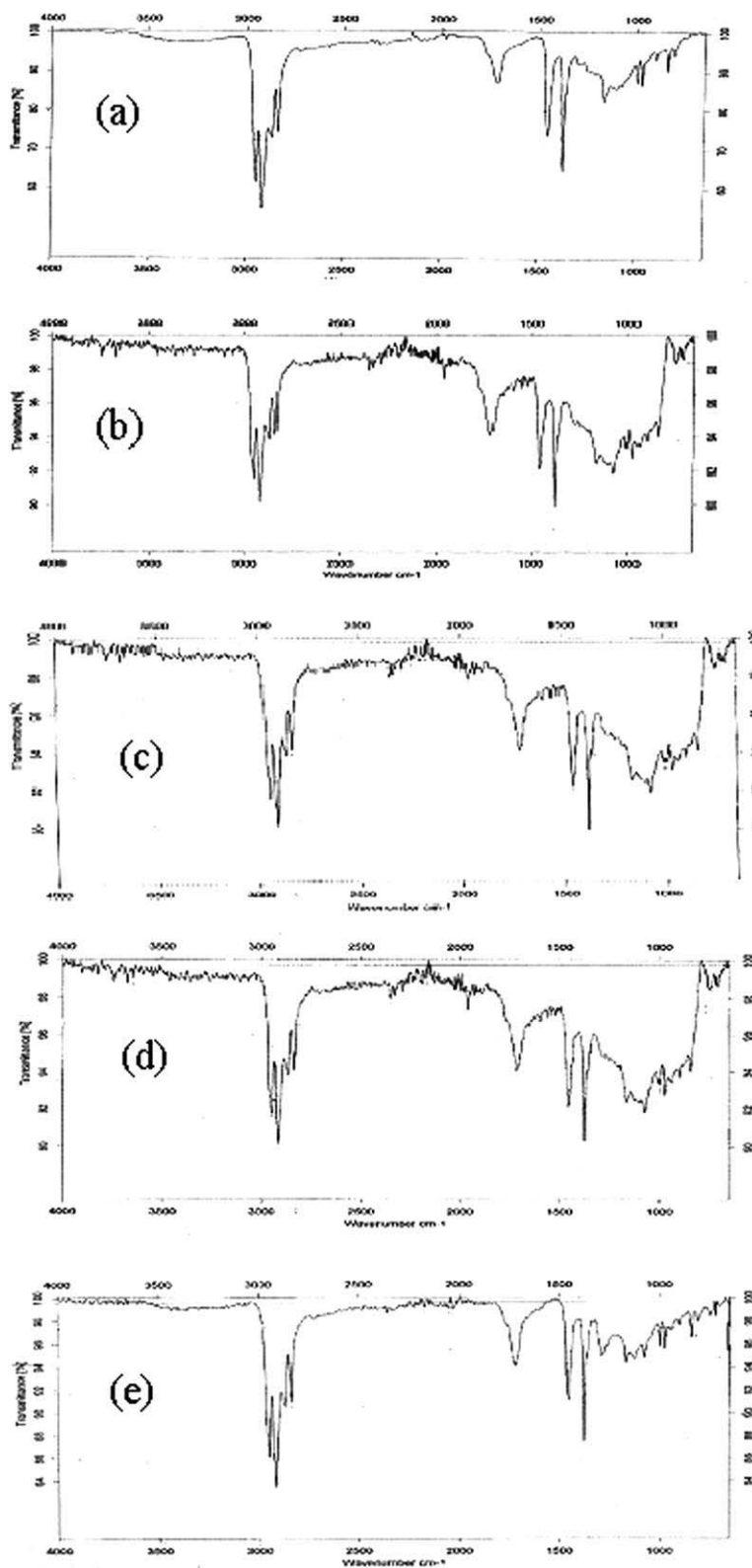

Figure 3   FTIR analysis of (a) blank composite **I,** (b) 20-kGy-irradiated composite **I,** (c) 40-kGy-irradiated composite **I,** (d) 60-kGy-irradiated composite **I,** and (e) 100-kGy-irradiated composite **I**.

Figure 4 FTIR analysis of (a) blank composite **II,** (b) 20-kGy-irradiated composite **II,** (c) 40-kGy-irradiated composite **II,** (d) 60-kGy-irradiated composite **II,** and (e) 100-kGy-irradiated composite **II.**

As shown in Figures 3–5, composites **I** and **II** were not stable, whereas composite **III** was the most stable. As was clearly shown in these spectra under these experimental conditions, irradiation affected the molecular structure of composites **I** and **II**. A steady increase in the intensity of the band at
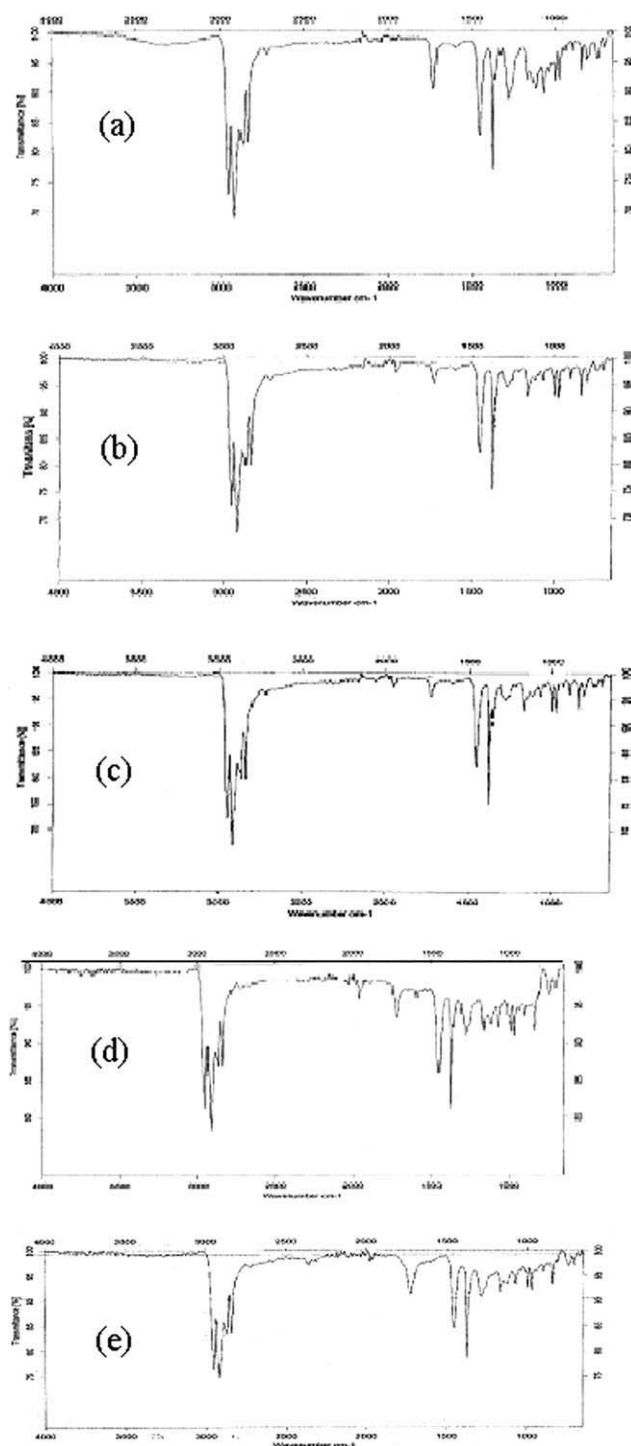
Figure 5 FTIR analysis of (a) blank composite **III,** (b) 20-kGy-irradiated composite **III,** (c) 40-kGy-irradiated composite **III,** (d) 60-kGy-irradiated composite **III,** and (e) 100-kGy-irradiated composite **III.**

1720 cm^{-1} indicated the formation of carbonyl groups, which corresponded to the production of aldehydes and ketones.

This could be explained by the fact that in the presence of air, oxygen reacts with the free radicals produced in the polymer matrix as a result of irradi-

ation; this leads to the formation of carbonyl groups.[46,47]

These results were in good agreement with those of Sevil and Guven,[48] who reported changes in the chemical structure of PP syringes corresponding to C=O (1720 cm^{-1}) and —OH (3400 cm^{-1}) after irradiation at doses between 25 and 100 kGy.

As shown in Figures 3–5, a band corresponding to —OH groups (3400 cm^{-1}) was not recorded. It seemed that under these experimental conditions, the concentration of —OH groups formed was not high enough to show up in the FTIR spectrum.

It was clear that composite **III** was the most stable because minor differences in the FTIR spectra were observed after the irradiation treatment. Therefore, the zinc Pc additives in the repeating units of composite **III** acted as stabilizing elements against γ irradiation because of the delocalization of excitation energy in the double and aromatic units. Also, because of the large ionic radius of Zn in composite **III** compared with composite **I** (metal-free) and composite **II** (containing Mg).

CONCLUSIONS

Composite films containing Pcs **3–5** were prepared successfully by the cast method. Good dispersion of the new Pcs **3–5** in PP was apparent, as shown by FTIR spectroscopy. They enhanced both the chemical and physical properties of PP simultaneously. Therefore, PP composites receive more attention, not only in industry but also in scientific society nowadays.

The prepared Pc composite films containing polymeric materials described previously meet the requirements of advanced technical and industrial applications.

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