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Radiation synthesis and characterization of zinc phthalocyanine composite based on 2-hydroxyethyl methacrylate/methyl methacrylate copolymer

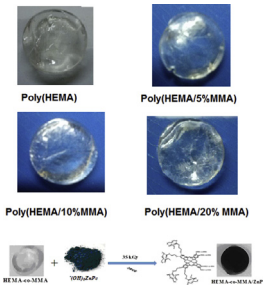
A.M. Abdel Ghaffar [a, *], Tamer E. Youssef [b, c], Hanan H. Mohamed [d]

[a] Radiation Research of Polymer Chemistry Department, Industrial Irradiation Division, National Center for Radiation Research and Technology, Atomic Energy Authority P.O. Box 29, Nasr City, Cairo, Egypt
[b] Applied Organic Chemistry Department, Chemical Industries Research Division, National Research Center, Dokki, Cairo, 12622, Egypt
[c] Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, P.O. Box 80204, Jeddah, 21589, Saudi Arabia
[d] Chemistry Department, Faculty of Science, Helwan University, Ain Helwan, Cairo, Egypt

HIGHLIGHTS

- The preparation of Poly(HEMA/MMA/ZnPc) by radiation forming modified composites.
- The low concentration of ZcPc (1 or 1.5 wt %) lead to form outstanding properties.
- These composites are a potential candidate for wide range of applications.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis and characterization of new 2-hydroxyethyl methacrylate-co-methyl methacrylate/zinc phthalocyanine composite Poly(HEMA/MMA/ZnPc) is described for the first time in this study. The aim of this research is to present possibility of radiation synthesis of the newly zinc phthalocyanine composites as potential candidates for wide range of applications. Gel (%) and swelling for Poly(hydroxyethyl methacrylate) Poly(HEMA) and the based Poly(hydroxyethyl methacrylate/methyl methacrylate) copolymer Poly(HEMA/MMA) with different composition 100/0, 95/5, 90/10 and 80/20 wt % were evaluated. It was found that Poly(HEMA/MMA) copolymer with composition 95/5 wt % characterized by its high swelling property at pH 7.4. The prepared composites **I** and **II** Poly(HEMA/MMA/ZnPc) with composition (95/5/1 wt%) and (95/5/1.5 wt%) respectively have been characterized by FTIR and TGA. The effect of gamma irradiation on the chemical properties of composite **I** was described. It is observed that the Zinc phthalocyanine with low concentration 1 wt % enhance chemical, thermal properties and stabilization against gamma radiation of the prepared composite **I**.

1. Introduction

Poly(2-hydroxyethylmethacrylate) Poly(HEMA) hydrogels have been widely described in literature as materials for biomedical

* Corresponding author.
E-mail address: am_abdelghaffar@yahoo.com (A.M. Abdel Ghaffar).

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applications. This is due to their high biocompatibility. However, a swollen Poly(HEMA) hydrogel has poor mechanical properties, lead to limited applications, such as for soft contact lenses or drug release carriers [1,2]. In addition, Poly(methyl methacrylate) Poly(MMA) is characterized by its highly transparent and high refractive index polymer [3,4]. Therefore copolymerization of Hydroxyethyl methacrylate with Methyl methacrylate result in forming copolymer has good physical, chemical and mechanical properties [5–7].

Previous reports showed that using of metallophthalocyanine to incorporate into several kinds of polymers forming polymer composites. These composites have widely utilized in the different fields of life, such as biomedical applications and materials sciences [8–11]. For example, attaching of sulfo-substituted cobalt(II) phthalocyanines to Poly(methyl methacrylate) or polypropylene matrix have been described previously [12].

A successfully polymerization via the incorporation of silicon(IV) phthalocyanine dichloride ($SiPcCl_2$) to the thermo-responsive PEG-methacrylates based polymers has been described for photodynamic therapy (PDT) application [13]. Wang et al. prepared a water-soluble Zinc phthalocyanine functionalized with 2-methylacrylic acid 6-(3,4-dicyano-phenoxy)-hexyl ester (MADCE). The resulted polymer composite has good singlet oxygen quantum yields for providing polymeric materials for photodynamic therapy applications [14]. The contribution of our group to this field of research has been quite remarkable and described in details in literature [15,16].

Therefore, incorporating of 2-Hydroxyethyl methacrylate/Methyl methacrylate copolymer Poly(HEMA/MMA) with zinc phthalocyanines compounds may be a most useful combination for wide range of applications such as non-linear optics, chemical sensors, semiconductors, liquid crystals, medical application, electrochromic devices, Langmuire Blodgett films, photochromic materials, and as photosensitizers for photodynamic therapy [17,18].

2. Experimental

2.1. Materials

Reagent grade hydroxyethyl methacrylate of purity 97.8% (Merck, Germany), methyl methacrylate of purity 99.9% (Merck, Germany), and other all reagent grade chemicals were used as received. The starting precursor 2,3,9,10,16,17,23,24-octamethylzincphthalocyanine (**1**) required for the synthesis of 2,3,9,10,16,17,23,24-octahydroxyzincphthalocyanine (**2**) was synthesized as reported in our previous work [19].

2.2. Preparation

2.2.1. Gamma irradiation

Radiation preparation of different copolymers and composites I and II Poly(HEMA/MMA/ZnPc) with composition (95/5/1 wt%) and (95/5/1.5 wt%) respectively in this study were preformed at a dose rate ranged from 0.79 to 0.65 Gy/sec in air using the ^{60}Co gamma cell facility of the National Center for Radiation Research and Technology, Cairo, Egypt.

2.2.2. Preparation of the Poly(HEMA/MMA) copolymers

The mixtures of 2-hydroxyethyl methacrylate and methyl methacrylate with different composition 100/0, 95/5, 90/10 and 80/20 wt % were prepared using methanol (80%) as a solvent. The prepared comonomer mixture was transferred to glass ampoules, sealed and subject to direct irradiation at dose 30 kGy, and dose rate 0.79 Gy/sec at ambient temperature.

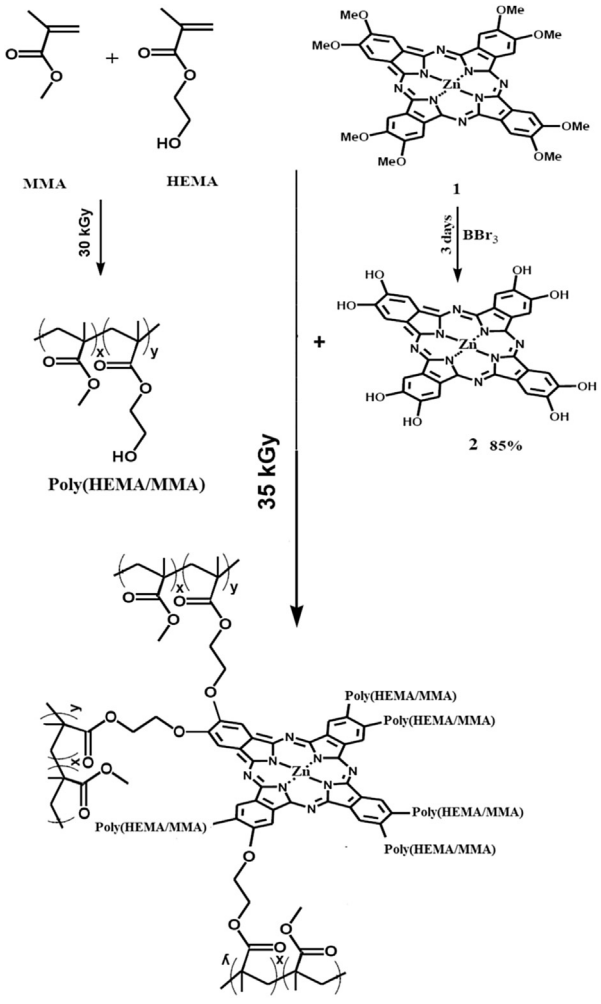
2.2.3. Preparation of 2,3,9,10,16,17,23,24-octahydroxyzincphthalocyanines [$(OH)_8$ZnPc]

The 2,3,9,10,16,17,23,24-octamethylzincphthalocyanine (**1**) was suspended in dichloromethane (100 mL) and BBr_3 (24 mL, 254 mmol) was added under N_2. The mixture was stirred for 3 days at room temperature, then methanol was added slowly and dark green suspension was formed. The suspended solution was centrifuged. The precipitated solids was filtered off, washed with methanol and dried under vacuum, to yield 85% of ZnPc **2**, as black green powder.

FTIR (KBr, cm^{-1}): 3313 (br-OH), 2956, 2920, 2855, 1654, 1544 (s),1468 (s), 1440 (m), 1322 (m), 1272 (m), 1140 (s), 1130, 920 (s), 880 (m), 753 (m). UV–Vis (DMF), λ_{max} (nm) 688, 622, 354. MS (FD): m/z 705.91 (M^+).

2.2.4. Preparation of Poly(HEMA/MMA/ZnPc) composites

To prepare composites **I** and **II**, Poly(HEMA/MMA/ZnPc) with composition (95/5/1 wt%) and (95/5/1.5 wt%) respectively, methanol (85%) used as a solvent. Before irradiation the mixture were stirred in magnetic stirring for 20 min. The mixtures were transferred to glass ampoules, sealed and subject to gamma radiation at dose 35 kGy, and dose rate 0.65 Gy/sec as shown in Scheme 1 [8,20].



Scheme 1. Preparation of Poly(HEMA/MMA/ZnPc) composites.