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Well-Controlled Emulsion Polymerization of Methyl Methacrylate Using (Hg,Cd)-Diphenylcarbazone Catalysts: An attempt to Create Hg-free, Nontoxic, γ-Radiation and thermal Stable Films

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Research Article

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Abstract

In this work, a procedure for synthesis of Hg and Cd-free PMMA films via emulsion polymerization using different concentrations (0.000025 - 0.00025 g mol/L) of Hg and Cd-diphenylcarbazone complexes (Hg(or Cd)DPC) as a catalytic chain transferring agent was reported. The extraction of either HgDPC or CdDPC from resultants polymers was confirmed using UV-Vis spectrophotometry and the neat polymers presented no cytotoxicity to human Hep G2 Cells. Well dispersity of PMMA (DPI of ca. 1.3) and the optimal performance in MMA polymerization was achieved using 0.00020 g mol/L HgDPC, which exhibited a PMMA yield of ca. 98%. Thermal behavior studies proved that PMMA films became highly thermally stable suggested as due to the elimination of head-to-head growing PMMA chains and disproportionation mechanistic steps. Therefore, the degradation process is mainly due to the random main chain scission, which on turn demonstrated a positive impact on its melting, decomposition and, glass transition (Tg) temperatures where, Tg of PMMA samples understudy increased in the following order: blank(60°C)@CdDPC(69°C)@HgDPC(84°C).The radiation shields and mechanical properties of PMMA films were also studied to evaluate the anti-radiation affinity of these complexes where, a tensile strength of 85.0 MPa of resultant PMMA using HgDPC was acquired.

1. Introduction

Free radical polymerization of some vinyl monomers such as methyl methacrylate (MMA) suffer the presence of mixture of chain structure and length. The presence of a small fraction of polymer chains that acquire head-to-head linkages, or unsaturated ends which are considered generally as thermally unstable that would initiate weak links and so forth to decompose into MMA monomer molecules below 300 °C. Such unzipping reaction negatively influence the polymer overall thermal stability that even though most of the polymer chains free defects are thermally stable at that temperature or higher [1, 2]. Therefore, the key to increase the thermal stability of the free radical polymerized polymethylmethacrylate (PMMA) is mainly to minimize the relative properties of weak links, head-to-head linkages or unsaturated chain ends towards suitability to complex with a variety of catalytic chain transferring agent to achieve an encouraging target of favorable polydispersity [3–5]. On the other hand, PMMA is said to be inert and non-toxic. However, it can contain varying amounts of residual MMA and catalysts such as benzoyl peroxide depending on the production method and polymer stability [6, 7]. The challenge is to establish a new catalytic polymerization processes to produce PMMA free of MMA and catalyst.

Catalytic polymerization of methyl methacrylate using organometallic compound as catalysts has been studied extensively in last 20 years. It is found that a huge divergence in PMMA structure and stability was acquired depend on the used central metals atom of organometallic compound [8]. Organometallic compounds that comprise of IIB metals are amusing because they own interesting coordination forms and structural features which come from d^{10} conformation [9]. Several Cd and Zn complexes have been investigated in the field of MMA polymerization [10–16]. Previously the effectiveness of alkyl- and aryl-Zn and Cd compounds *in polymerization of MMA was investigated* [10]. Recently, Cd and Zn complexes containing ancillary ligands, pyridyl-imines and N-substituted 2-iminoalkylpyridines have been applied for

MMA polymerization [11–16]. N,N-di(2-picolyl) cyclohexylamine based Zn (II), and Cd(II) complexes were found to be active catalysts for the MMA polymerization to produce syndiotactic PMMA [11]. Nayab and his coworkers have also been investigated the performance of Cd(II) and Zn (II) complexes with bispyridylamine, iminopyridine and 2-iminoalkylpyridines derivatives in MMA polymerization [12–15]. Moreover, they have been synthesized Cd (II) and Zn(II) containing 4-bromo-N-(2-pyridinylmethylene) benzenamine and N-methyl-N-((pyridine-2-yl)methyl) benzeneamine ligands [15, 16]. It was clear from polymerization data that Zn(II) complexes resulted in higher activity at 60°C compared to the Cd(II) cognate under same experimental conditions [16]. However, wider polydispersity indexes of produced PMMA ranged from 2.33 to 2.58 were observed. In addition, syndio-enriched (67–68%) PMMA has been yielded with all the synthesized complexes, disregarding of their coordination forms and catalytic activities. It is also evident that the syndiotacticity was not sufficiently affected by change of the metal center carrying same ligand framework. Even though mechanical properties of PMMA polymer are an essential factor to identify the suitability of polymer for a variety of engineering applications however, the mechanical properties of the PMMA materials obtained by using these Zn and Cd complexes were not reported [17, 18].

On the other hand, the catalytic performance of group IIB metals (viz., Zn, Cd, and Hg) diphenylcarbazone complexes (MDPC) was investigated in bulk polymerization of MMA [5, 19]. The MDPC exhibited good performance in MMA conversion, but the resultant polymers were contaminated by these toxic complexes. However, the promising results (viz., thermal, and mechanical properties) of applying of Zn carbazone in the bulk polymerization of MMA as catalysts [5], encouraged us to investigate the catalytic performance of Hg and Cd carbazone in polymerization of MMA. In contrast to zinc and cadmium, mercury has a stable monovalent oxidation state, and thus exhibits an appreciable chemistry as Hg(I) and Hg(II), which are stable in aqueous environment [20]. Even though, the mercury compounds are used in several applications especially as catalysts [21–23]. However, for the toxicity reason the use of mercury has declined significantly in recent years [24, 25].

In this study, the catalytic performance of M(Cd and Hg)DPC was investigated in MMA polymerization. We have been tried to overcome the presence of Cd and Hg in the resultant PMMA by applying emulsion polymerization [26]. In addition, an extraction method was applied to remove the remained MDPC in the resultant PMMA and the separation of MDPC from polymer was verified by using UV-Vis spectrophotometry. Moreover, the cytotoxicity of resultant neat PMMA was investigated using human Hep G2 cells. The fact that our objective is not limited only to produce specific PMMA but also to shed a light to process which can be used for polymerization of other vinyl monomer. On the other hand, we have been tried to develop a more sustainable route to improve the polymer thermal, mechanical and radiation shielding properties. The thermal stability profiles of PMMA synthesized in presence of the metals (Cd and Hg) diphenylcarbazone, particularly mercury, were assessed functionally as to enhance its application even further at elevated temperatures.

2. Experimental

2.1. Synthesis of Materials

2.1.1. Synthesis of Diphenylcarbazone (DPC)

Diphenylcarbazone was prepared by the oxidation of diphenylcarbazide (ACS reagent grade (Sigma-Aldrich 259225)) with 3% hydrogen peroxide in alcoholic potassium hydroxide [27]. On neutralization and recrystallization, the red-orange mixture of both diphenylcarbazone and diphenylcarbazide was obtained. This product was treated with sodium carbonate in hot ethanol and diphenylcarbazide was extracted with ether. Then acidification of the aqueous solution with hydrochloric acid produced a red powder melting at 127° which is pure diphenylcarbazone [27, 28].

2.1.2. Synthesis of Hg and Cd Diphenylcarbazone Complexes

Solutions of the mercury and cadmium perchlorate salts, in an alcohol-water mixture (20:80, v/v) react immediately with solutions of diphenylcarbazone in the same solvent to form blue/violet color in the case of mercury and pink color in the case of cadmium complexes [29–32]. The concentrations of both reagent and salts were 0.002 g mol/L for each cation. The pH had to be chosen at a special value, for Hg complex pH was adjusted at 3.0 using citric acid and sodium phosphate dibasic (Na₂HPO₄) buffer (0.2 M) while, for Cd complex pH was adjusted at 7.5 using acetic acid and sodium acetate buffer (0.2 M). In both two cases the complex solutions show the Tyndall effect, and the colloids particles were flocculated on addition of sodium nitrate electrolyte. After about 30 min to await complete flocculation, the precipitate was filtrated, and then washed with 96% ethanol and water. The precipitated complexes were kept in dark and dried over night at room temperature with this precipitate the polymerization reactions were performed.

As shown in Fig. S1(a) the UV – visible spectrum of the mercury dipenylcarbazone exhibited the characteristic band of Hg(II)DPC at ca. 558 nm [29, 30]. In addition, a shoulder 460–528 nm detected in the same spectrum, may characterize the Hg(I)DPC [29, 30]. On the other hand, the spectrum of cadmium diphenylcarbazone shows a broad peak centered at 482 nm. [30], which may be linked with the formation of Cd(II)DPC (Fig. S1(b)). Moreover, similar bands characteristic of Hg(II)DPC, Hg(I)DPC, and Cd(II)DPC were observed in the resultant PMMA solutions (Fig. S1 (a and b)).

2.2. Synthesis of polymethyl methacrylate.

2.2.1. Catalytic Polymerization Reaction

The main purpose of the using emulsion polymerization of MMA method in presence of either HgDPC or CdDPC as catalysts is that the most of diphenylcarbazone complexes were transferred to the filtrates and the remained complexes in PMMA films were removed. All other chemicals used were of ACS reagent grade (Sigma-Aldrich). 1.0 mL of Polysorbate 80 as emulsifier was mixed with 0.5 mL of 0.1 M ammonium persulfate solution and dissolved in 100 ml distilled water. The solution was charged in a 500

ml three-necked round flask isolated from light. The round flask was fitted with condenser in water bath at 70°C with continuous magnetic stirring. Then 15 grams of inhibitor-free methyl methacrylate monomer were mixed with the two metal diphenylcarbazone complexes separately at various concentrations (0.000025 to 0.00025 g mol/L) in dry glass ampoules. When the temperature of the round flask reached 70 °C, the monomer was charged from one neck to the flask with continuous stirring, the color of solution was changed depending on the type of metal complex, and the reaction mixture was subjected to reflux for 4 hours. After the elapsed time, the flask was left to cool to ambient temperature and then the polymer formed was precipitated using 95% dry methanol. Polymer precipitate was dried in vacuum at 65°C overnight until constant weight then polymer yield (wt.%) was measured.

2.2.2. Removal of Diphenylcarbazone Complexes from Polymer

Cd and Hg diphenyl carbazone extraction from different polymer materials was carried out by soaking PMMA polymer precipitate (as prepared in Sect. 4.2.1) in 200 mL toluene 25°C for 14 days, the experiment was carried out in darkened glassware. Polymer formed was precipitated using methanol-water mixture (20:80 v/v). First the, the non-flocculated complex colloidal solution was decanted and then polymer was filtrated using Whatman filter grade 541 paper where, the complexes particles form colloidal solutions as is obvious from the Tyndall-effect and they suspended in filtrate [29, 30]. The separation of complex from polymer was followed by measuring the decrease in absorbance of complex remained in treated polymer in toluene solution after each run by using UV-Vis *spectrophotometer* in the wavelength range 400 to 700 nm (Fig. S1) where the complexes obey Beer's law in the concentration range used. The steps above were repeated 2 to 5 times. In addition, to verify the presence or absence of Hg in polymer (PMMA) after carrying out extraction experiment, Hg was measured using HgDPC of concentration in the range between 0.000025 and 0.0002 g mole/L. However, the PMMA film prepared using HgDPC of 0.00025 g mole/L showed the presence of 0.038 mg mol/L Hg after applying removal process.

2.2.3. Preparation of Polymethylmethacrylate Film.

Finally, PMMA polymer films with a thickness of ~1 mm, were prepared by casting the Hg and Cd free polymer solutions into a clean glass Petri dish (10-cm diameter), left to dry under ambient condition for 24h, then placed in a vacuum oven at 70 °C to remove any residual solvent.

2.3. Cytotoxicity Assessment of PMMA solution.

The study of cytotoxic activity of polymer was performed using Hepatocellular carcinoma (HePG-2) cell line [33–36]. The cell line was obtained from ATCC via Holding company for biological products and vaccines (VACSERA), Cairo, Egypt. The cell line mentioned above was used to determine the inhibitory effects of compounds on cell growth using the MTT assay. This colorimetric assay is based on the conversion of the yellow tetrazolium bromide (MTT) to a purple formazan derivative by mitochondrial succinate dehydrogenase in viable cells. Doxorubicin was used as a control anticancer drug for comparison. The PMMA solution in dimethyl sulfoxide (DMSO) of different concentrations (viz., 1.56 and

3.125 μ g/mL) (prepared from polymer films (see Sect. 4.3.2)), were disinfected with 15 ml of phosphate buffer solution (PBS) (containing potassium chloride and potassium phosphate) and an antibiotic (a mixture of Penicillin G Potassium and Streptomycin Sulphate) for 30 minutes, as suggested in literature [34]. Hep G2 Cell Line human was grown in RPMI-1640 medium - containing 10% fetal bovine serum. Then antibiotics (100 units/ml penicillin and 100 μ g/mL streptomycin) were added, and the cell line was seeded in a 96-well plate at a density of 1.0x10⁴ cells/well and cultured in a humidified incubator filled with 5% CO₂/95% air mixture at 37°C for 48 h. After incubation, the cells were treated with different concentration of polymer solutions and incubated for 24 h. The cell culture assay was done triplicate. After the designated incubation time, the cytotoxicity activity was evaluated using MTT assay to check cell viability as described in literature [35]. Next, 20 μ l of thiazolyl blue tetrazolium bromide solution (MTT, Sigma) in DMEM-LG (5mg/mL) was added, and the plate was incubated in the dark for 4 hours at 37°C. The MTT solution was removed, and 100 μ l of DMSO was added into each well to dissolve the purple formazan formed. The colorimetric assay was measured and recorded at absorbance of 570 nm using a plate reader (EXL 800, USA). The relative cell viability in percentage was calculated as (A570 of treated samples/A570 of untreated sample) X 100.

2.4. Gamma (g)- irradiation.

Different polymeric samples under investigation were irradiated to different doses of g-radiation using ⁶⁰Co gamma source at the National Center for Radiation Research and Technology, Nasr city, Cairo. The gamma irradiation was carried out in atmospheric air at a dose rate of 0.45 Mrads/h.

2.5. PMMA Films characterization.

The molecular weights (Mw and Mn) of the polymer samples and their polydispersity were determined using Gel permeation chromatography (see results in Fig. S2 as an example) (Agilent GPC 1100 series, Germany, PL gel 100, 1000, 100000 on series and the porosity of 5 micrometers and refractive index detector). Thermogravimetric studies (TGA) studies were carried out for all polymer samples using LINSIES analyzer (STA PT 1600). About 10 mg of polymer samples were tested at temperature range of 30° to 800 °C under nitrogen atmosphere with a flow rate of 50.0 ml/min and a heating rate of 5 °C/min. From the TGA results, differential thermogravimetric plots (DTG) were calculated as the first derivatives of the TGA curves. Differential scanning calorimetry (DSC) The thermal transition behavior of all prepared samples was determined by Differential Scanning Calorimetry model netzsch DSC 200F3 over a temperature range from ambient up to 500° C with a heating rate of 20 °C/min under a nitrogen gas at a flow rate of 50.0 ml/min. ¹H-NMR analysis were carried out by using Spectro spin-Brucker AC 200 MHz NMR Spectrometer. Mechanical properties: tensile strength (TS) and percentage tensile elongation at break (E) of the films were determined at room temperature using EMIC universal testing machine model DL10000, in general accordance with ASTM D638. Data for yield strength and elongation at break were obtained in tests executed at a crosshead speed of 10 mm/min. An EMIC extensometer, having a gage length of 25 mm, was used. Between 10 and 15. Mercury was measured using a cold vapor method with a Perkin Elmer Mercury Hybrid system (MHS-10). Analysis was carried out according to procedures in the

operator's manual. Ultraviolet–visible spectroscopy (UV-Vis) measurements were performed using Thermo Fisher Scientific Evolution 300 spectrophotometer.

3. Results And Discussion

3.1. Yield, Molecular Weight and Polydispersity of PMMA

The change of the yield of emulsion polymerization of MMA with concentration of both CdDPC and HgDPC catalysts are depicted in Fig. 1. In general, the presence of diphenylcarbazone complexes enhanced the percentage yields of PMMA from 47% of blank up to 84% and 98% in the case of CdDPC and HgDPC at 0.00015 and 0.00020 g mol/L, respectively. As shown, percentage yield increased with increasing Cd complex concentration reached a maximum value at 0.00015 g mol/L, followed by a significant decrease up to 0.00025 g mol/L. However, percentage yield increased with increasing Hg complex concentration in the range between 0.00015 and 0.00020 g mol/L. Also, it is clear from Fig. 1 that HgDPC was the most suitable one for production of PMMA which exhibited a yield to PMMA of 98% with a concentration of 0.0002 g mol/L at 70 °C. According to *UV-visible results (see Fig.15)* it appears that the observed higher performance of HgDPC to PMMA than CdDPC can be attributed to the coexistence of Hg(I)DPC together with Hg(II)DPC in the complex. Which may be promoted Hg(I)/Hg(II) redox reaction for enhancing free radical catalytic chain transferring polymerization of MMA in liquid phase. However, further study seems to be still needed to confirm such suggestion.

The number average and weight average molecular weights of the PMMA films were measured using Gel permeation chromatography and are represented graphically in Fig. 2. As revealed, CdDPC start to increase the number average molecular weight of PMMA passing through a maximum at 0.00005 g mol/L followed by a significant decrease and these decreases increased gradually with concentration. While in case of HgDPC, the number average molecular weight showed a slow decreasing with increasing complex concentration. The weight average molecular weight in both cases showed rapid deceases in values and then remained almost constant up to concentration 0.00025 g mol/L in the case of HgDPC.

The polydispersity of all polymer samples prepared by emulsion technique are calculated and represented in Fig. 3. As presented, and the most interesting results is that using CdDPC or HgDPC catalysts, PMMA prepare films were assured of better polydispersity indexes at the different concentration and generally at about 1.30 and 1.36 respectively, for high concentration (0.0002 g mol/L). In addition, the obtained polydispersity index of PMMA in this study is still much better than that one reported by Park et al. and Cho et al. in literature [15,16]. From the above achieved results, it is evident that Hg and Cd diphenylcarbazone complexes proved of having a selective catalytic activity on the rate propagation and termination steps through the emulsion polymerization of MMA.

3.2. Thermogravimetric analysis

Thermogravimetric analysis of native PMMA prepared film and those prepared in presence of CdDPC or HgDPC complexes under nitrogen atmosphere are represented in Fig.s 4 and 5. From these profiles, we

can conclude that, PMMA removed firstly water content and/or residual solvent below ~ 120 °C which is hardly visible. At higher temperatures, the pure polymeric material starts to degrade in three major steps. The first one proceeds from T_{onest} @ 120 °C up to T_{end1} @ 200 °C which can be attributed to the scissions of head-to-head linkages. The second step proceeds from T_{end1} up to T_{end2} @ 290 °C due to scissions of unsaturated chain ends which formed during disproportionation. The third step proceeds from T_{end2} up to T_{end3} @ 380 °C due to random scissions of the most resisting polymer chains to thermal degradation which are quite agree to those reported earlier [37].

A significant influence on the thermal degradation of PMMA films; prepared in presence of both CdDPC or HgDPC complexes, especially at high complex concentration, whereas, the first step of degradation is completely absent, Fig.s 4 and 5. Also, the respective peculiar temperatures are shifted to higher values with increasing the residual material depending on the type and concentration of the complex.³ This can be attributed to the presence of both complexes that enhance the thermal resistance of PMMA films. These results were confirmed by DTG thermograms of all samples, Fig.s 6 and 7. As shown, pure PMMA films exhibited the three decomposition peaks (DTG_{max1}, DTG_{max2} and DTG_{max3}) at @ 145, 240 and 340 °C. PMMA films prepared in presence of CdDPC complex and at low concentration (0.000025 g mol/L) illustrated that the first step is completely absent which means that the elimination head-to-head linkages through the termination step. The second and third steps, which assigned mainly to the unsaturated ends and the random scissions within the polymer chains are shifted to high temperature @ 280 and 390 °C with a lower mass loss rate. At a higher complex concentration (0.00005) to 0.00025 g mol/L), the first two steps are completely absent, with a much lower mass loss rate at the third peak (DTG_{max3}) with a higher shift up to 410, 460, 500, 560 and 590 °C (Fig. 6). By using HgDPC instead of CdDPC, Fig. 7, the first two steps were completely absent at all concentrations. For the third peak (DTG_{max3}), a much lower mass loss rate occurs with a higher shift up to 670 °C at 0.00025 g mol/L. From the above results we can concluded that, the presence of these complexes through the emulsion polymerization of MMA enhancing the thermal stability of PMMA films which can attributed to its catalytic role on the termination step which decrease the head-to-head linkages and number of unsaturated ends [5,38].

3.3. Differential scanning calorimetry

DSC is most usually used to delimit the transition temperatures of a polymeric material such as glass or melting transitions. However, it measures only the total heat flow and the sum of all thermal transitions. In addition to associated enthalpy for each process [39]. The thermal properties of PMMA samples were examined by DSC to estimate how the thermal transitions of these samples are affected due to the presence of CdDPC or HgDPC complexes through the polymerization process. Fig. 8 illustrates the DSC thermogram of pure PMMA film and that in presence of 0.000025 g mol/L CdDPC or HgDPC. The measurements from the DSC for all samples are presented in Table 1.

From Fig. 8 and Table 1 we can conclude that the increasing of the glass transition temperature (Tg) of PMMA of films is mainly due to organization role played by CdDPC and HgDPC complexes through the

emulsion polymerization process. Such venture can be attributed to a reduced mobility action imposed by plausible crosslinking [40]. In addition, the two major endothermic peaks observed at 238 and 317 °C are mainly depicted to the decomposition of pure PMMA sample. These endothermic peaks slightly shifted towards higher values due to the presence of diphenylcarbazone complexes. The decomposition temperature of any polymeric material depends on its purity, molecular weight, and crystallinity and as an affirmed deduction the highest the crystallinity the higher the decomposition or degradation temperature [41]. The changes in heat of fusion and increase of the melting temperatures can suggest that the crystallinity and perfection of the crystal structure are reduced with increased of cross-linking [41].

The generation of new exothermic peaks at ~ 285 and 310°C in the presence of CdDPC and HgDPC, respectively indicates the nonoxidative in character which appear to play an important role in the formation of structure features that retard the flammability, resembling dehydration and cross-linking actions, especially in the case of HgDPC [42,43]. Around 450 °C, a large exotherm appear for all polymer samples under investigation due to oxidative reactions of the polymeric material and combustion of the char residue, moreover, it is indicated from the acquired results that the addition of CdDPC or HgDPC to MMA through emulsion polymerization augments their thermal stability which agrees with previously reported results [44].

3.4. g-ray degradation and protection efficiency

The effect of gamma irradiation on PMMA prepared in the presence and absence of diphenylcarbazone complexes were investigated at 0.5, 1.5, 2.5, 5.0, 7.5, and 10.0 Mrads. The weight loss was calculated and the results of which are represented in Fig.s 9 and 10 [45]. Pure PMMA clearly showed a high degree of degradation as exposed to g-ray with nearly complete destruction at 10.0 Mra ds. On the contrary, those prepared in presence of diphenylcarbazone complexes gained diverse degree of protection. To clarify the effect of g-ray on the of all PMMA films tacticity were followed up using ¹H NMR spectroscopy. The stereoregularity of all samples were determined from the intensity of the peaks shifted at d (ppm) 0.85, 1.02, and 1.21 for syndiotacticity, heterotacticity, and isotacticity, respectively Fig. S3) and the results are given in Table 2. As revealed, pure PMMA showed a 68.2% heterotacticity which indicated that it is nearly amorphous [26]. In the presence of cadmium and mercury complexes, the tacticity of all samples was significantly improved as shown in Table 2, reducing in turn the amorphous region that is the most susceptible for all physical and chemical interactions and degradation compared to the crystalline region [45]. The overall results clearly indicate the direct outcome of the carbazone complexes role as catalyst and regulator during the emulsion polymerization of MMA which enrich the prepared polymers with an explicated effectiveness against radiation.

3.5. Mechanical properties

Fig.s 11 and 12 depict the mechanical properties, in term of tensile strength and elongation at break, for all PMMA films under investigation. It is evident that presence of CdDPC or HgDPC complexes during the emulsion polymerization process significantly improved the mechanical properties of PMMA films.

Whereas an increase in tensile strength 85.0 and 90.0 MPa in the case of PMMA produced using 0.0020 and 0.0025 g mol/L HgDPC respectively was observed and consequent decrease in elongation at break as the concentration of both complexes increased. These results can support the fact of the generated inter-crystalline links between lamellae that is regarded as a main reason for these deeds [46,47]. According to mechanical properties results, it can thus be suggested that the resultant PMMA in this work can be used in bone cement as intraocular and as screw in bone fixation and in acrylic glass manufacture because it has both good transparency and high fracture (tensile) strength compared with that one reported in other studies in literature (48 to 76 MPa) [48-51].

3.6. Hg Cytotoxicity of PMMA films.

The cytotoxicity results (Fig. 13) indicated that the 1.56 μ g/mL solution of PMMA films synthesized using HgDPC complex of concentration in the range between 0.00005 to 0.00025 g mol/L, in dimethyl sulfoxide (DMSO), presented no cytotoxicity to hepG2 cells with cell viability values of 100%. However, the 3.125 μ g/mL solution PMMA film synthesized using HgDPC complex of concentration of 0.00020 and 0.00025 g mol/L exhibited cytotoxicity of ca. 3.2 and 9%, respectively. On the other hand, PMMA solutions (1.56 μ g/mL PMMA in DMSO) of films synthesized using different concentration of CdDPC complex (0.00005 to 0.00025 g mol/L) did not also show cytotoxicity to HepG2 cells with cell viability of 100% however, the 3.125 μ g/mL solution of PMMA film synthesized using CdDPC complex of concentration of 0.00025 exhibited only cytotoxicity of ca. 2.0 (Fig. S4). Which can be attributed to stronger interaction of Hg complex with MMA than Cd complex.

4. Conclusions

The results in this study, clearly demonstrated that the controlled emulsion polymerization of methyl methacrylate using mercury diphenylcarbazone, as a catalytic chain transferring, in producing of polymeric films free of hazardous Hg with excellent thermal and radiation stability. Where, Hg complex exhibited higher performance in conversion of methyl methacrylate to PMMA polymer than Cd complex.

TG and DTG results indicated that using diphenylcarbazone complexes eliminated head-to-head chains and unsaturated ends consequently, the degradation process of PMMA became resistant up to higher temperatures compared to that of natively prepared polymer. The higher thermal stability of PMMA films prepared in the presence of these complexes can be attributed to the role of diphenylcarbazone complex in controlling the polymerization process to get more ordered polymer; so that, preventing quick and full diffusion of the heat into the polymeric material. In addition, DSC investigation, also proved the glass transition temperature uphill from 60.0 up to 70.0 °C for CdDPC and up to 84.0 °C for HgDPC. The superiority of mercury can be attributed to its highest molecular weight polymer that reflects positively on its stability. Yet, Tg of 84.0 °C for HgDPC catalyst is still lower than that one founded by by Park et al. and Cho et al. [15,16], namely, Tg of ca. 130.0 °C for the Cd and Zn containing 4-bromo-N-(2-pyridinylmethylene) benzenamine and N-methyl-N-((pyridine-2-yl) methyl) benzeneamine complexes.

However, from the polymerization data reported in these previous studies, it is also clear that the Tg value is little higher than that one (i.e., 120°C) recorded for the blank sample [15,16].

Furthermore, study of g-irradiation effect on the PMMA films stability and the subsequent direct impact on the mechanical characteristics displayed the positive role of diphenylcarbazone complexes in producing a significant increase in both shielding and tensile strength of PMMA films compared to pure polymer films. This indicating the role of these complexes as catalytic regulator which is positively reflected on its crystallinity and negatively reflected on its elongation at break [52].

Declarations

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References

[1] R. I. Acosta, K. C. Gross, G. P. Perram, Thermal degradation of poly(methylmethacrylate) with a 1.064 μm Nd:YAG laser in a buoyant flow. Polym. Degrad. Stab. **121**, 78-89 (2015).

[2] G. Moad, D.H. Solomon, *The chemistry of radical polymerization*, 2nd edn. (Elsevier Ltd., 2006).

[3] E. Cao, Z. Tan, S. Sun, Z. Liu, H. Zhang. Enhancing the thermal stability of poly(methyl methacrylate) by removing the chains with weak links in a continuous polymerization. Polym. Degrad. Stab. **96**, 2209-2214 (2011).

[4] N. Patra, M. Salerno, M. Malerba, P. D. Cozzoli, A. Athanassiou. Improvement of thermal stability of poly(methyl methacrylate) by incorporation of colloidal TiO₂ nanorods. Polym. Degrad. Stab. **96**, 1377-1381 (2011).

[5] E.H. El-Mosallamy. Enhancing the thermal and mechanical parameters of PMMA using zinc diphenylcarbazone complex as the initiator. J. Therm. Anal. Calorim. **115**, 707-711 (2014).

[6] International Association for Research on Cancer (IARC). *IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans,* Vol. 19, (France, Lyon, 1979), pp. 187-194.

[7] O. P. Gautschi, C. L. Schlett, J.-Y. Fournier, D. Cadosch. Laboratory confirmed polymethyl-methacrylate (Palacos®)-hypersensitivity after cranioplasty. Clin Neurol Neurosurg. **112**, 915-916 (2010).

[8] I. Kim, J.-M. Hwang, J. K. Lee, C. S. Ha, S. I. Woo. Polymerization of methyl methacrylate with Ni(II)a-Diimine/MAO and Fe(II) and Co(II) pyridyl bis(imine)/MAO. Macromol. Rapid. Commun. **24**, 508–511 (2003).

[9] C. E. Housecroft, A. G. Sharpe, *Inorganic Chemistry*, 3rd edn. (Prentice Hall, 2008).

[10] R. G. Compoton, *Comprehensive chemical kinetics mechanism and kinetics of addition polymerizations*. Vol. 31, eds.: M. Kucera, (Elsiever, Amsterdam, 1992) pp. 109-112.

[11] Y. Song, D. Kim, H. -J. Lee, H. Lee. Synthesis and structural characterization of $[(dpca)MX_2]$ (M = Cu, X = Cl; M = Cd, X = Br and M = Zn, X = NO₃) complexes containing *N*,*N*-di(2-picolyl)cyclohexylamine (dpca) and their application to methyl methacrylate polymerization. Inorg. Chem. Commun. 45, 66-70 (2014).

[12] S. Shin, S. H. Ahn, M. J. Jung, S. Nayab, H. Lee. Synthesis, structure and methyl methacrylate polymerization of cobalt(II), zinc(II) and cadmium(II) complexes with N,N',N-bidentate versus N,N',N-tridentate N,N',N-bis((1Hpyrazol-1-yl)methyl)amines. J. Coord. Chem. **69**, 2391-2402 (2016).

[13] S. H. Ahn, J. Shin, S. Nayab, H. Lee. Polymerization of methyl methacrylate catalyzed by Co(ii), Cu(ii), and Zn(ii) complexes bearing N-methyl-N-((pyridin-2-yl)methyl) cyclohexanamine. Bull. Korean Chem. Soc. **37**, 763-766 (2016).

[14] Y. Song, D. Kim, H.-J. Lee, H. Lee. Cd(II) and Zn(II) Complexes containing N,N'-bidentate N-(pyridin-2ylmethylene) cyclopentanamine: synthesis, characterisation and methyl methacrylate polymerisation. Bull. Korean Chem. Soc. **35**, 2929-2934 (2014).

[15] S. Park, J. Lee, H. Lee, A. R. Jeong, K. S. Min, S. Nayab. Five-coordinate dinuclar cobalt (II), copper (II), zinc (II) and cadmium (II) complexes with 4-bromo-N-(2-pyridinylmethylene) benzenamine: Synthesis, characterisation and methyl methacrylate polymerization. Appl. Organometal Chem. 33, e4766 (2019).

[16] H. Cho, M. J. Jung, J. Jeon, H. Lee, S. Nayab. Synthesis, structural characterization and MMA polymerization studies of dimeric 5-coordinate copper(II), cadmium(II), and monomeric 4-coordinate zinc(II) complexes supported by N-methyl-N-((pyridine-2-yl)methyl) benzeneamine. Inorganica Chimica Acta. 487, 221–227 (2019).

[17] L. J. Gibson, M.F. Ashby, *Cellularsolids structure and properties*, 2nd edn. (Cambridge University Press: Cambridge, 1997).

[18] J. Brandrup, E. H. Immergut. *Polymer Handbook,* eds. E. A. Grulke, 4th edn. (Wiley: New York 1999).

[19] E.H. El-Mosallamy, Prospective influence of catalytic chain transfer polymerization of methyl methacrylate via metal carbazone complexes. Macromol. Indian J. **9**, 1-7 (2013).

[20] D. C. Bebout. Mercury, In Inorganic & Coordination Chemistry, Encyclopedia of Inorganic Chemistry. John Wiley & Sons: New Jersey. 2006.

[21] M. Nishizawa, H. Imagawa, H. Yamamoto. A new catalyst for organic synthesis: mercuric triflate.Org. Biomol. Chem. **8**, 511-521 (2010).

[22] M. Eckert, G. Fleschmann, R. Jira, H. M. Bolt, K. Golka. *In Ullmann's Encyclopedia of Industrial Chemistry* (VCH: Weinheim, 2006) pp. 191-207.

[23] H. Yamamoto, I. Sasaki, Y. Hirai, K. Namba, H. Imagawa. M. Nishizawa, Silaphenylmercuric triflate catalyzed reactions: synthesis of a solid supported salt catalyst. Angew. Chem. Int. Ed. **48**, 1244-1247 (2009).

[24] T. W. Clarkson, L. Magos, G. J. Myers. N. Engl. The toxicology of mercury–Current exposures and clinical manifestations. J. Med. **349**, 1731–1737 (2003).

[25] R. A. Bernhoft, Mercury toxicity and treatment: A review of the literature, J. Environ. Public Health., **2012**, article ID 460508 (2012). https://doi.org/10.1155/2012/460508.

[26] C.S. Chen, Prog. Emulsion polymerization mechanisms. Polym. Sci. **31**, 443-486 (2006).

[27] K. H. Slotta, K. R. Jacobi. Herstellung organischer Reagenzien im analytischen Laboratorium. I. Diphenyl-carbazid und Diphenyl-carbazon. Anal. Chem. **77**, 344-348 (1929).

[28] a) P. Krumholz, E. Krumholz. Zur Kenntnis des Diphenylcarbazons. Monatsh **70**, 431-436 (1937); b) J.J.R.F. Da Silva, J.C.G. Calado, M.L. De Moura. Separation of commercial diphenylcarbazone into its components. Talanta **11**, 983-984 (1964).

[29] S. Balt, E. Van Dalen. The reaction of diphenylcarbazide and dipenylcarbazone with cations. Part III. Nature and Properties of the mercury complexes. Anal. Chim. Acta **27**, 416-421 (1962).

[30] S. Balt, E. Van Dalen. The reaction of diphenylcarbazide and dipenylcarbazone with cations. Part IV. Cations of Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb. Anal. Chim. Acta **27**, 466-471 (1962).

[31] H. M. V. Swamy, S. B. Sajjanar, A. H. M. Siddalingaiah. Studies on some lanthanide (III) complexes of o-, m- and p-chloro substituted diphenylcarbazones. Indian J. Chem. A **39**, 1150-1156 (2000).

[32] R. T. Pflaum, L. C. Howick. The Chromium-diphenylcarbazide reaction. Am. Chem. Soc. **78**, 4862–4866 (1956).

[33] H. Wang, B. Chen, M. He, X. Yu, B. Hu. Selenocystine against methyl mercury cytotoxicity in Hep G2 cells. Sci. Rep. <u>7: 147, 1-8 (2017).</u> https://doi.org/10.1038/s41598-017-00231-7

[34] L. Z. Linan, N. M. N. Lima, C. Benatti, M. Xavier, A. A. Rodrigues, F. Manenti, A. Jardini, R. M. Filho, R. Gilioli. Cytotoxicity assessment of a poly(methyl methacrylate) synthesized for the direct fabrication of bone tissues. Braz. Arch. Biol. Technol. **61**, e18160526 (2018).

[35] a) J. C.; Stockert, A.; Blázquez-Castro, M. Cañete, R. W. Horobin, A. Villanueva. MTT assay for cell viability: Intracellular localization of the formazan product is in lipid droplets". Acta Histochemica. Acta Histochemica. **114**, 785–96 (2012); b) T. Mosmann, Rapid colorimetric assay for cellular growth and survival: application to proliferation and cytotoxicity assays. J. Immunol. Methods **65**, 55–63 (1983).

[36] P. E. Feuser, P. C. Gaspar, E. Ricci-Júnior, M. C. S. da Silva, M. Nele, C. Sayer, P. H. H. de Araújo. Synthesis and characterization of poly(methyl methacrylate) PMMA and evaluation of cytotoxicity for biomedical application. Macromol. Symp. **343**, 65-69 (2014).

[37] G. Zhang, J. Zhang, F. Wang, H. Li. Thermal decomposition and kinetics studies on the poly (2,2dinitropropyl acrylate) and 2,2-dinitropropyl acrylate-2,2-dinitrobutyl acrylate copolymer. J. Therm. Anal. Calorim. **122**, 419-426 (2015).

[38] G. Choong, D. De Focatiis. A method for the determination and correction of the effect of thermal degradation on the viscoelastic properties of degradable polymers. Polym. Degrad. Stab. **130** 182-188 (2016).

[39] W. G. Osiris, M. T. H. Moselhey. Thermal and structure studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends. Nat. Sci. 4, 272-280 (2012).

[40] C. C. Wei, D. Esposito, K. Tauer. Thermal and structure studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends. Thermal properties of thermoplastic polymers: Influence of polymer structure and procedure of radical polymerization. Polym. Degrad. Stab. **131**, (2016) 157-168.

[41] J. Guan, C. Guoqiang. Copolymerization modification of silk fabric with organo phosphorous flame retardant. Fire Mater. **37**, 261-270 (2009).

[42] N. A. El-Zaher, M. A. Melegy, O.W. Guirguis. Thermal and structure analyses of PMMA/TiO₂ nanoparticles composites. Nat. Sci. **6**, 859-870 (2014).

[43] Z. Dobkowski, E. Rudnik, Lifetime prediction for polymers via the temperature of initial decomposition, part 2. J. Therm. Anal. Calorim. **69**, 693-697 (2002).

[44] W. G. Osiris, S. M. Mohamed, N. A. El-Zaher. Macrostructure and optical study of PMMA/TiO₂ nanoparticles composites. NSNTAIJ. **7**, 60-65 (2013).

[45] S. M. Sayyah, A. B. Khaliel, H. M. Abd El-Salam. Molecular weight studies of the g-radiation degradation of poly(methyl methacrylate) doped with poly(p-sulfanilamide). J. Appl. Polym. Sci. **106**, 1294 -1300 (2007).

[46] J. Li, R. A. Shanks, Y. Long. Mechanical properties and morphology of polyethylene–polypropylene blends with controlled thermal history. J. Appl. Polym. Sci. **76**, 1151-1164 (2000).

[47] L. Klapiszewski, K. Bula, M. Sobczak, T. Jesionowski. Influence of processing conditions on the thermal stability and mechanical properties of PP/silica-lignin composites. Int. J. Polym. Sci. **2016**, 1–12 (2016).

[48] N. Dunne, J. Clements, J-S. Wang, *Acrylic cements for bone fixation. In Joint Replacement Technology*, eds. P. A. Revell, 2nd edn. (Woodhead: Cambridge, UK, 2014) pp. 212-256.

[49] S. Samavedi, L. K. Poindexter, M. Van Dyke, A. S. Goldstein, *Chapter 7 - Synthetic biomaterials for regenerative medicine applications, In* Regenerative Medicine Applications in Organ Transplantation, eds.
G. Orlando, J. Lerut, S. Soker, R. J. Stratta, (Academic Press, Elsiever, Amsterdam, 2014) pp. 81-99.

[50] M. Mahmoudian, A. P. Marjani, R. Hasanzadeh, M. Moradian, S. M. Shishavan. Optimization of mechanical properties of in situ polymerized poly(methyl methacrylate)/alumina nanoparticles nanocomposites using Taguchi approach. Polym. Bull. **77**, 2837-2854 (2020).

[51] Massachusetts Institute of Technology Home Page (www.mit.edu). http://www.mit.edu/~6.777/matprops/pmma.htm (accessed May 14, 2021).

[52] P. Krishnaiah, C. T. Ratnam, S. Manickam. Enhancements in crystallinity, thermal stability, tensile modulus and strength of sisal fibers and their PP composites induced by the synergistic effects of alkali and high intensity ultrasound (HIU) treatments. Ultrason. Sonochem. **34**, 729-742 (2017).

Tables

Table 1: Values of transition temperatures and associated heat of fusion for PMMA films.

Concentration		Tg (°C)	1 st endothermic peak		2 nd endothermic peak		exothermic peak	
(g mol/L)			Peak temp.	Heat release	Peak temp.	Heat release	Peak temp.	Heat release
			(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)
3⁄4		60	238	-36.53	317	-15.62	3⁄4	3⁄4
CdDPC	2.5´10 ⁻ 5	65	250	-45.31	325	-25.35	285	17.28
	5.0´10 ⁻ 5	66	254	-39.22	326	-27.21	287	19.11
	10.0 ´10 ⁻⁵	66	255	-41.44	329	-28.65	288	20.21
	15.0 ´10 ⁻⁵	68	259	-41.62	327	-26.13	291	20.67
	20.0 ´10 ⁻⁵	70	266	-44.25	331	-30.71	299	21.55
	25.0 ´10 ⁻⁵	69	271	-46.55	334	-30.92	298	18.22
HgDPC	2.5′10⁻ ₅	70	260	-49.92	337	-21.62	310	13.55
	5.0´10 ⁻ 5	72	265	-52.56	342	-25.55	315	17.43
	10.0 ´10 ⁻⁵	75	269	-55.71	346	-27.11	317	18.26
	15.0 ´10 ⁻⁵	79	275	-57.42	345	-30.31	320	18.05
	20.0 ´10 ⁻⁵	82	274	-57.11	351	-28.56	319	21.83
	25.0 ´10 ⁻⁵	84	277	-60.20	366	-32.91	329	22.66

Table 2: Variation of PMMA tacticity with metal diphenylcarbazone complexes. The stereoregularity (%) of all samples were determined from the intensity of ¹H NMR peaks shifted at d (ppm) 0.85, 1.02, and 1.21 for syndiotacticity, heterotacticity, and isotacticity, respectively.

Concentra	ation	Syndiotactic	Heterotactic	Isotactic
g mol/L		(%)	(%)	(%)
Blank		26.6	68.4	5.0
CdDPC	2.5´10 ⁻⁵	45.7	45.6	8.7
	5.0´10 ⁻⁵	49.4	41.2	9.4
	10.0´10 ⁻⁵	54.2	33.1	12.7
	15.0´10 ⁻⁵	49.9	37.2	12.9
	20.0´10 ⁻⁵	55.3	36.7	8.0
	25.0´10 ⁻⁵	48.1	37.5	14.4
HgDPC	2.5´10 ⁻⁵	47.5	42.2	10.3
	5.0´10 ⁻⁵	48.4	38.5	13.1
	10.0´10 ⁻⁵	51.6	33.9	14.5
	15.0´10 ⁻⁵	53.2	31.7	15.1
	20.0´10 ⁻⁵	60.4	35.0	4.6
	25.0´10 ⁻⁵	52.2	33.3	14.5





Effect of Hg and Cd diphenylcarbazone concentration on the yield of polymethyl methacrylate.



Effect of Hg and Cd diphenylcarbazone concentration on the weight average (Mw) and number average (Mn) molecular weights of polymethyl methacrylate.



Effect of Hg and Cd diphenylcarbazone concentration on the dispersity of polymethyl methacrylate.



TG thermograms of PMMA films prepared in presence of different concentration of CdDPC complex.



TG thermograms of PMMA films prepared in presence of different concentration of HgDPC complex.



DTG thermograms of PMMA films prepared in presence of different concentration of CdDPC complex.





DTG thermograms of PMMA films prepared in presence of different concentration of HgDPC complex.



DSC analysis of PMMA films prepared in presence and absence of CdDPC and HgDPC complexes.



Weight loss versus the irradiation dose for PMMA films prepared in presence of different concentration of CdDPC complex.



Weight loss versus the irradiation dose for PMMA films prepared in presence of different concentration of HgDPC complex.



Effect of Hg and Cd diphenylcarbazone concentration on the tensile strength of PMMA films.



Effect of Hg and Cd diphenylcarbazone concentration on the elongation at break of PMMA films.



Concentration of HgDPC complex as a catalyst. Using different concentration of PMMA in DMSO (Red bar: $1.56 \mu g/mL$ and blue bar: $3.125 \mu g/mL$).

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