

Synthesis of Stable PMMA Against γ -Irradiation and Thermal Degradation Using Cobalt Tetraphenyl Porphyrin Catalyst

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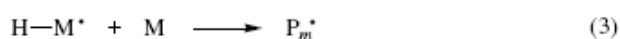
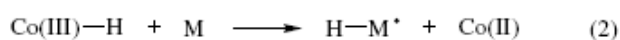
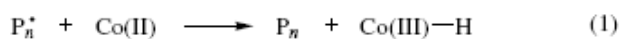
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ABSTRACT

Poly methyl methacrylate (PMMA) was synthesized using different concentrations of cobalt tetraphenyl porphyrin (CoTPP) as a catalyst in presence of sodium bisulphite (NaHSO₃) as an initiator. The molecular weights and stability of the polymers against degradation by thermal and γ -radiation tools were investigated. (Fourier transform infra red) FT-IR, gel permeation chromatography (GPC) and thermal gravimetric analysis (TGA) were used as tools for structure confirmation, molecular weights determination and polymer resistance to degradation. The convincingly reported results indicate the ability of such polymers to resist both thermal and radiation effects compared with pure polymer.

1. INTRODUCTION

The concept of catalytic chain transfer (CCT) emerged in the early 1980s denoted that certain low-spin cobalt (II) porphyrin complexes are adequate as catalysts and regulators to control polymers molecular weight during free-radical polymerizations of methacrylates¹⁻³. Subsequent to these initial reports, a number of studies were also reported that CCT with cobalt complexes is highly effective for controlling the molecular weight of these polymers based on α -methyl substituted monomers^{4,5} (e.g., methacrylates), monosubstituted monomers^{6,7} (e.g., styrene's, acrylates, acrylamide), and copolymers involving these monomers⁸⁻¹⁰. The main three factors that make this form of chain transfer attractive are: (1) catalytic mode of action of the cobalt complex, (2) high transfer constant of the cobalt complex, and (3) polymers prepared should possess a C=C end group. The kinetics and mechanism of the CCT process are reported in many studies.¹¹⁻¹⁵. The process is generally believed to occur in two steps as depicted in Scheme 1. The first step involves the transfer of a hydrogen atom from a propagating radical to the Co (II) complex to form a polymer and a cobalt (III) hydride. In the second step, reaction of the cobalt (III) hydride with monomer yields a monomeric radical, which continues propagation, (step 3) and regenerates the cobalt (II) complex.^{2, 16}



Scheme 1. Mechanism of catalytic chain transfer by Co (II) complexes.

Cobalt (II) porphyrins were identified amongst the first class of cobalt (II) complexes utilized as catalytic chain transfer agents (CCTA) ². However, due to the difficulty of synthesis, poor stability, and poor solubility in polar media, and the highly colored nature of these complexes, different chelates were subsequently developed.^{17, 18}

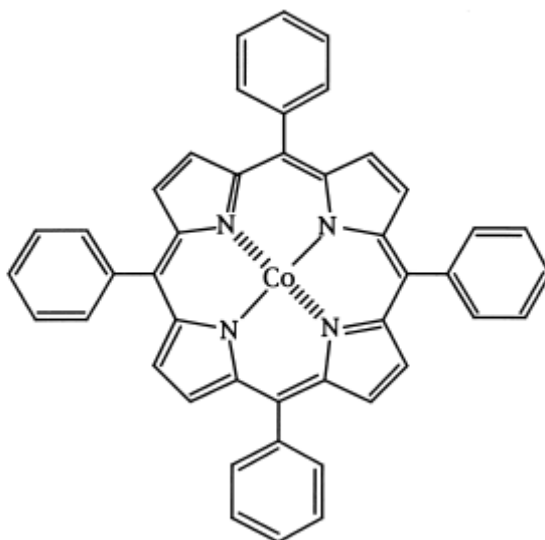


Figure 1: Cobalt tetraphenyl porphyrin (CoTPP)

In the present work, PMMA was prepared in presence of CoTPP as a catalyst and NaHSO₃ as an initiator at range of concentrations of CoTPP to develop highly resistant polymers towards thermal and radiation degradation atmospheres. Polymer structure validity and average molecular weights were evaluated before and after degradation and the protection percentage were calculated.

2.1. MATERIALS AND METHODS

The chemicals used were supplied as follows: Deactivated methyl methacrylate monomer (MMA) 99% Aldrich. Acetone > 99.5% Fluka Chemie GmbH. Sodium bisulphite > 95% ADWIC El-Nasr pharmaceutical chemicals Co. Methanol > 99.8% Fluka chemie GmbH. Toluene > 99.5% Reidel- de Haen Co.

The monomer was activated before use by shaking with sodium hydroxide and kept under anhydrous Sodium sulphate while solvents were distilled appropriately and kept dry prior use.

2.2. Solution polymerization procedure:

The polymerization mixture is made by mixing of MMA monomer, CoTPP solution (soluble in acetone) in different concentrations ranging from $1 \times 10^{-5} \text{M}$ to $6.5 \times 10^{-5} \text{M}$, acetone (solvent) and sodium bisulphite as the initiator (0.05 ml of 0.1M solution in distilled water) were placed in a glass ampoule then degassed using liquid nitrogen and finally sealed under the flow of purified dry nitrogen gas. All ampoules were then heated at 84 C for 8 hours.

2. 3. Techniques:

FT-IR (Fourier transform infra red Spectroscopy): Nicolet 6700Thermo-Scientific. Gel Permeation Chromatography (GPC): Agilent GPC 1100 Series, Germany, PL gel 100, 10000,100000 on series, and the porosity is 5 micrometers and refractive index detector. Thermal gravimetric analyzer (TGA): Shimadzu-50, made in Japan, atmosphere: N₂, rate: 5 degrees/minute. γ -radiation source: The samples were irradiated with the ⁶⁰ Russian irradiation facility gamma rays at a dose rate 10. kGy/h. The irradiation facility was constructed by the National Center for Radiation Research and Technology, Atomic Energy Authority of Egypt.

3. RESULTS AND DISCUSSION

3.1. PMMA structure confirmation:

Figure (2) illustrates the FT-IR spectra for some selected samples of PMMA (C₃, C₅ and C₇) that represents the general trend of the reaction, including the blank sample. The spectra profile confirms the PMMA structure at its characteristic bands clearly proved with a mixed polymer tacticity.

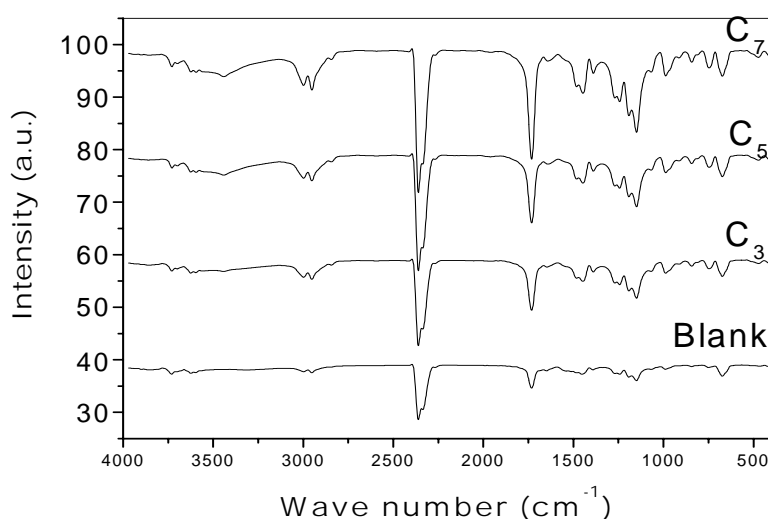


Figure 2: FT-IR spectra for pure PMMA and catalyzed PMMA samples

3.2. Conversion and CoTPP concentration relationship profile:

The overall results of polymer conversion % (= polymer weight/ monomer weight X 100), values of number average (M_n) and weight average (M_w) molecular weights at each catalyst concentration and the polydispersity index are reported in table 1. The pattern of conversion, figure (3), shows a volcano-shaped curve which indicates that CoTPP has an activation/deactivation behaviour depending on its concentration. It is also noticed that lower concentrations of CoTPP exhibit an activation towards polymerization progress reaching a maximum value of 86.14% conversion at CoTPP concentration of 3×10^{-5} moles/L. The higher concentrations are evident to retard the conversion of the monomer due to an apparent deactivation that could be attributed to the higher population of the catalyst molecules and a subsequent steric hindrance of the bulky structure of the CoTPP.

Polycrystalline metal-tetraphenyl porphyrins and phthalocyanines were found to inhibit the polymerization process.¹⁹

Table 1: Conversion % of PMMA, number and weight average molecular weight and polydispersity related to CoTPP concentration.

Sample	CoTPP conc.(mole/L)	conversion %	Mn	Mw	Poly Dispersity (PD)
Blank	0	22.47	5.03 X10 ⁵	6.97 X10 ⁵	1.3849
C ₁	1 X10 ⁻⁵	40.98	9.84 X10 ⁴	3.94 X10 ⁵	2.1553
C ₂	2 X10 ⁻⁵	72.27	7.61 X10 ⁴	2.15 X10 ⁵	2.8319
C ₃	3 X10 ⁻⁵	86.14	3.31 X10 ⁴	1.11 X10 ⁵	3.3558
C ₄	4 X10 ⁻⁵	50.21	2.17 X10 ⁴	8.83 X10 ⁴	3.9965
C ₅	4.5 X10 ⁻⁵	17.4	1.17 X10 ⁴	6.27 X10 ⁴	5.3478
C ₆	5.5 X10 ⁻⁵	12.3	2.43 X10 ⁴	5.05 X10 ⁴	2.079
C ₇	6.5 X10 ⁻⁵	9.55	1.88 X10 ⁴	2.98 X10 ⁴	1.5856

- Initiator concentration (NaHSO₃) for all samples = 0.1 M
- M_n = number average molecular weight
- M_w = weight average molecular weight

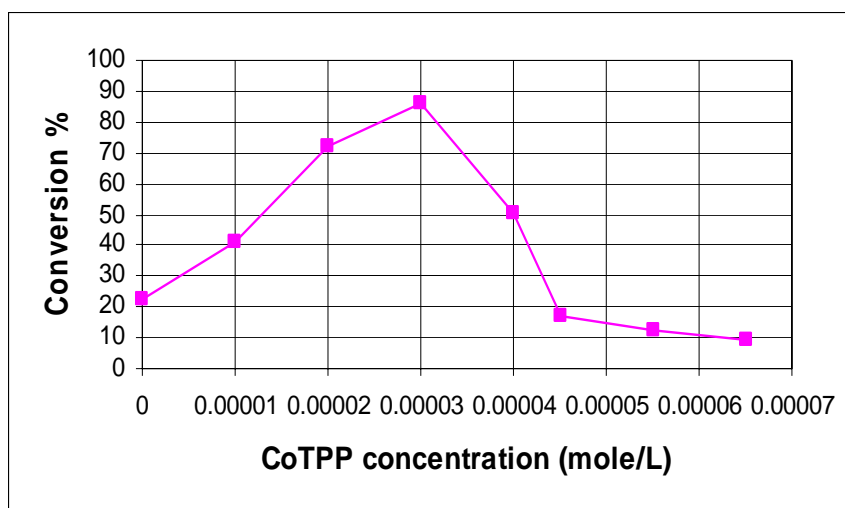


Figure 3: Relation between the CoTPP concentrations and PMMA conversion %

This behaviour supports the existence of redox-initiated mechanism enhanced by presence of HSO₃⁻ cocatalyst-initiator.¹⁹ Such type of relationship shown in figure (3) suggests strongly that the reaction follows two different reaction mechanisms for each mode of polymerization progress. The first step of activation could be explained as due to a

progressive effect of the Co TPP catalyst and the deactivation due to the loss of its activity through its regeneration to its native inactive mode^{2, 16}.

3.3. Thermal and γ -radiation degradation:

To study PMMA structural stability against progressive heat, all samples were subjected to heat up to 600°C using TGA technique. The results showed comparative improvement for samples C₁ to C₇ as compared to the blank sample that prepared in absence of CoTPP (figure 4). All samples exhibit a first stage of weight loss at a temperature range of 110 °C – 130 °C, which could be attributed to the removal of physically adsorbed water. The blank sample started to degrade – after the first stage – at 236.01 °C, while C₁-C₇ samples started to degrade with a mere 20 °C delayed effect with the most resistant sample at 265.91 °C (sample C₃, CoTPP concentration = 3×10^{-5} M). The behaviour of increased thermal stability could well be due to increased polymeric chains packing mode.

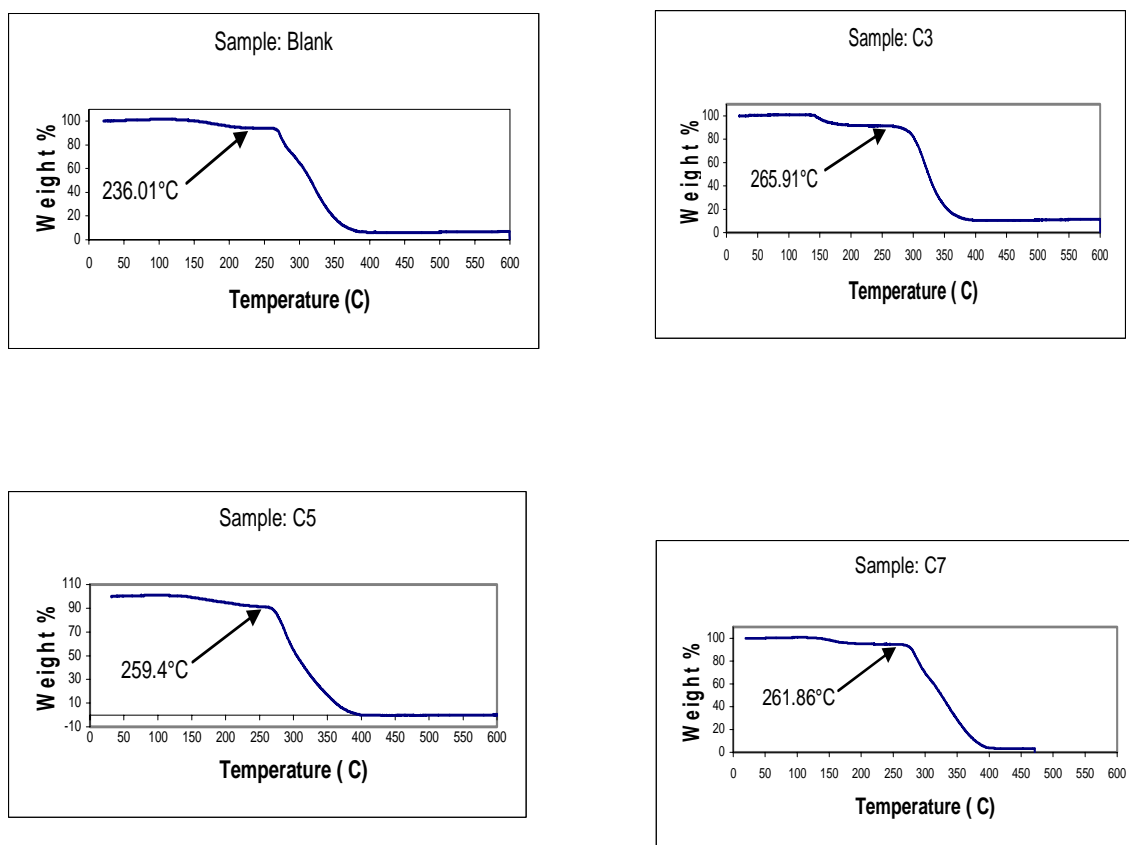


Figure 4: Thermogravimetric (TG) studies of selected PMMA samples

The degradation effect of γ -radiation on pure and catalyzed PMMA samples, at a total dose of 5 M rads is summarized in table (2). Whereas, the blank PMMA suffered great depreciation to its number and weight average molecular weight values (about 60% overall degradation); C₁-C₇ samples, however, exhibited a respectable overall resistance to degradation with a maximum protection at CoTPP concentration of 3×10^{-5} M (sample C₃).

Table 2: Depreciation values to PMMA number and weight average values before and after γ -radiation

Sample	CoTPP conc.(mole/L)	Mn before radiation	Mn after radiation	Mw before radiation	Mw after radiation
Blank	0	5.03×10^5	1.94×10^5	6.97×10^5	4.87×10^5
C ₁	1×10^{-5}	9.84×10^4	6.08×10^4	3.94×10^5	2.96×10^5
C ₂	2×10^{-5}	7.61×10^4	5.95×10^4	2.15×10^5	1.67×10^5
C ₃	3×10^{-5}	3.31×10^4	3.40×10^4	1.11×10^5	1.14×10^5
C ₄	4×10^{-5}	2.17×10^4	2.42×10^4	8.83×10^4	8.94×10^4
C ₅	4.5×10^{-5}	1.17×10^4	1.37×10^4	6.27×10^4	6.18×10^4
C ₆	5.5×10^{-5}	2.43×10^4	1.97×10^4	5.05×10^4	4.32×10^4
C ₇	6.5×10^{-5}	1.88×10^4	1.68×10^4	2.98×10^4	2.81×10^4

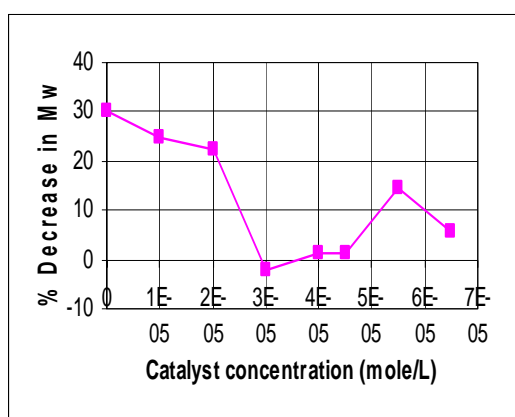


Figure 5: Effect of γ -radiation on percent depreciation weight average molecular weight

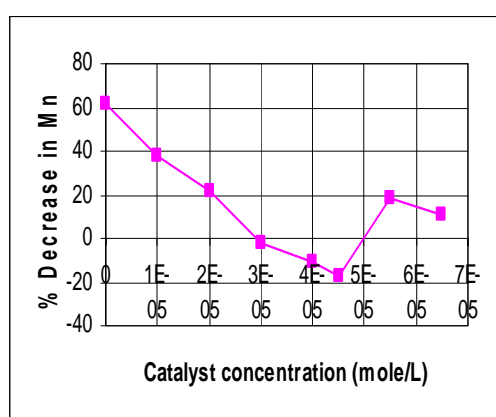


Figure 6: Effect of γ -radiation on percent depreciation number average molecular weight

Figures (5 & 6) illustrate the graphical representation of the γ -radiation degradation effect on both the number and weight average molecular weights. As observed in both figures (5 & 6), the number average molecular weight is more susceptible to degradation when compared with the weight average molecular weight parameter indicating the presence of the chains in a weak bonding state with the complex compound molecules.²⁰

In conclusion, PMMA prepared in presence of CoTPP at different concentrations evidenced an increased protection for the polymers against heat, with a mere 20°C higher than that of the pure PMMA (prepared in absence of CoTPP), which could be explained as due to polymeric chains packed structure. Increased structural stability was also noticed against γ -radiation at a dose = 5 Mrads, with a maximum stability at CoTPP concentration of 3×10^{-5} M (zero degradation) compared to pure PMMA. The stability could be explained as due to the increased PMMA tacticity towards the isotactic structure and the role of the catalyst in protecting its degradation by shielding the polymeric chains from being affected by the γ -radiation at that dose of 5 rads.

4. References

1. Smirnov, B. R.; Belgovskii, I. M.; Ponomarev, G. V.; Marchenko, A. and Enikolopyan, N. S. (1980) Dokl. Akad. Nauk SSSR. 254:127.
2. Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V. and Belgovskii, I. M. (1981) J. Polym. Sci., Polym. Chem. Ed. 19:879.
3. Smirnov, B. R.; Plotnikov, V. D.; Ozerkovskii, B. V.; Roshchupkin, V. and Enikolopyan, N. S. (1981) Polym. Sci. USSR 23: 2807.
4. Davis, T. P.; Haddleton, D. M. and Richards, S. N. (1994) J. Macromol. Sci., Rev. Macromol. Chem. Phys. C34:274.
5. Davis, T. P.; Kukulj, D.; Haddleton, D. M. and Maloney, D. R. (1995) Trends Polym. Sci. 3:365.
6. Martchenko, A.; Bremner, T. and O'Driscoll, K. F. (1997) Eur. Polym. J. 33:713.
7. Chiefari, J.; Moad, C. L.; Moad, G. and Rizzardo, E. Macromolecules (in press).
8. Greuel, M. P. and Harwood, H. J. (1990) Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.) 32:545.
9. Ittel, S. D.; Gridnev, A. A.; Moad, C. L.; Moad, G.; Rizzardo, E. and Wilczek, L. WO 9731:030 [(1997) Chem. Abstr. 128:234752].
10. Chiefari, J.; Jeffery, J.; Mayadunne, R. T. A.; Moad, G.; Rizzardo, E. and Thang, S. H. (2000) ACS Symp. Ser. 768:297.
11. Karmilova, L. V.; Ponomarev, G. V.; Smirnov, B. R. and Belgovskii, I. M. (1984) Russ. Chem. Rev. 53:132.
12. Mironichev, V. Y.; Mogilevich, M. M.; Smirnov, B. R.; Shapiro, Y. Y. and Golikov, I. V. (1986) Polym. Sci. USSR (Engl. Transl.) 28:2103.
13. Gridnev, A. A. (1989) Polym. Sci. USSR (Engl. Transl.) 31:2369.
14. Gridnev, A. A. (1992) Polym. J 24:613.
15. Davis, T. P. and Kukulj, D. (1995) Macromol. Theory Simul. 4:195.
16. Sanayai, R. A. and O'Driscoll, K. F. (1989) J. Macromol. Sci. -Chem. A26:1137.
17. Burczyk, A. F.; O'Driscoll, K. F. and Rempel, G. L. (1984) J. Polym. Sci., Polym. Chem. Ed. 22:3255.
18. Carlson, G. M. and Abbey, K. J. (1985) U. S. Patent 4:526:945.
19. Sadek, E. M.; Mekkewi, M. A.; Yehia, F. Z.; Solyman, S. M. and Hassan, S. A. (2001) J. Macromol. Chem. Phys. 202:1505.
20. Aida, T. and Inoue, S. (2000) "The Porphyrin Handbook". Academic Press., 6:176.