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Prospective influence of catalytic chain transfer polymerization of methyl methacrylate via metal carbazone complexes

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ABSTRACT

Catalytic chain transfer polymerization via metal carbazone of Zn (II), Cd (II), and Hg (II) is a very efficient and versatile free-radical polymerization technique for the synthesis of poly (methyl methacrylate). The process is based on the ability of the carbazone to motivate the chain transfer to monomer molecules and as has been reported earlier producing reliable feature of controlled polymerization with well-controlled process. Continuing the efforts to reveal more insights into supplementary advantageous concepts when using metal carbazones as initiators and chain transfer agents, the curing role of such is meant to be investigated as a promising perception for advanced applications.

KEYWORDS

Chain transfer;
Metal complex;
Polymerization;
Dispersity;
Crystallinity.

INTRODUCTION

The molecular weight distribution of a polymer determines basically the properties of the final product; whereas high molecular weight polymer chains are required for imparting strength to the final product, low molecular weight chains are required for easy flow in polymer processing[1,2]. Free radical polymerization produces usually low molecular weight polymers which are commonly prepared in presence of chain transfer agents such as thiols or carbon halides[3,4].

In 1980s, Smirnov's et al[5,6] revealed that certain low-spin Co (II) complexes are able to catalyze the chain transfer to monomer polymerization reactions, hence providing a possible mean for molecular weight control. Proceeded and continuous work exposed that certain organometallic complexes presence during the polymerization processes, most notably those of chromium and molybdenum, are causing molecular weight reductions and their further impact on the polymer physical characteristics[7,8]. In the present work, metal carbazone complex compounds were used as an additive through the polymerization of methyl methacrylate monomer where their rule as transferring and curing agents are to be assessed.

EXPERIMENTAL

Materials

The stabilized methyl methacrylate monomer was supplied by Aldrich. When activated (inhibitor free) refractive index measurement was run to affirm purity prior use[9].

Zinc, cadmium and mercury carbazone complexes were prepared as reported with affirmed structure[10]. Pure-grade toluene was used as a solvent for the polymer.

Polymerization process and film formation

15 gram of inhibitor-free monomer was mixed with the three metal complexes separately at various concentrations in a dry glass ampoules and sealed under flow of purified and dry nitrogen gas, and then, placed in an adjusted electric oven at 80 °C for 24 hours. After which the ampoules were left to cool to ambient temperature and then broken to release its contents under toluene. The polymer solution was cost onto glass dishes to form transparent films with a thickness of ~1 mm. The cast films were dried under ambient condition for 24h and then placed in a vacuum oven at 70 °C to remove any residual solvent. The conversion yield% was calculated as the ratio of polymer weight compared to monomer weight used.

Polymer characterization

The molecular weights of the polymer samples and their polydispersity values were determined using Gel permeation chromatography (Agilent GPC 1100 series, Germany, PL gel 100, 1000, 100000 on series and the porosity of 5 micrometers and refractive index detector). The polymer structure was confirmed using Nicolet 380 FT-IR spectrophotometer. The crystallinity of polymethyl methacrylate samples were investigated using x-ray diffractometer (JSX-60PA-TEOL and Ni-filtered CuK$_\alpha$ radiation). The x-ray patterns of the samples were recorded automatically with a scanning speed of 2°/min, and the scanning angular range (2θ) from 5 to 50°.

RESULTS AND DISCUSSION

Conversion yield, molecular weight and dispersity

The conversion yield of methyl methacrylate monomers to polymer in the presence of Zn, Cd, and Hg carbazone extended from 70 to 97% and as shown in Figure 1 (fairly close to that of pure polymer of 86%). The pattern of conversion % shows, in general, a volcano-shaped profile which visualizes a critical concentration for maximum activity of the carbazone complex compound as a catalyst for such polymerization process. It is also noticed that a gradual increase of the complex concentration is accompanied by gradual increase of the polymer conversion % till that peak of maximum activity at a concentration of 4.4×10^{-5}, 1.18×10^{-4} and 1.86×10^{-4} g mol/L for Zn, Cd and Hg carbazone complexes, then deactivates at higher concentrations due may be to an apparent crowding of its higher population and the subsequent steric hindrance of the bulky complex.

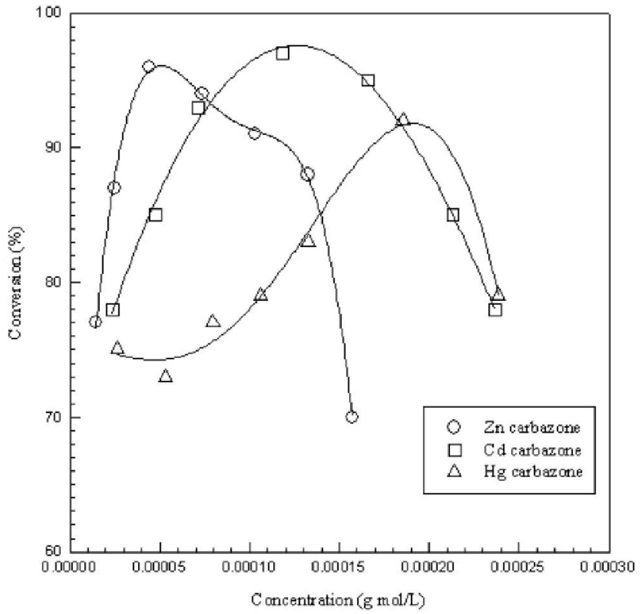


Figure 1 : Effect of metal carbazone complexes concentration on the conversion %

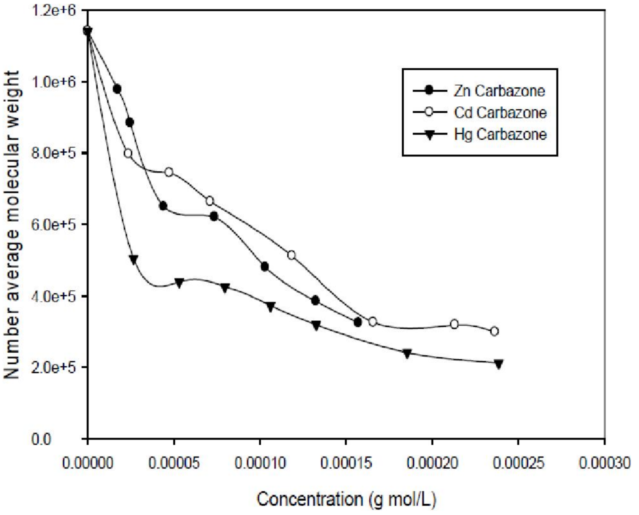


Figure 2 : Effect of metal carbazone complexes concentration on the number average molecular weight

Molecular weight measured values of PMMA prepared in the presence of different metal complexes suffered preferential reduction and as shown in Figures 2-

3. The molecular weight parameters of weight and numbers were found to increase as the complex concentrations was increased[11,12]. The polydispersity profile was also recorded where it is included to be influenced by the complex type and concentration and as evidenced from Figure 4. The polydispersity profile illustrates that an improvement in the polydispersity, preferentially according to metal type and its concentration, which could be attributed to the ability of different metal carbazone complexes to cap the free radicals, produced probably, due to the monomer π bond rupturing during the polymerization process, via its azo group producing a hydrazo form which is accompanied by a color change. In this case, the hydrazo form is used as a new active center for the polymerization process that yields a polymer with lower dispersity values[13,14].

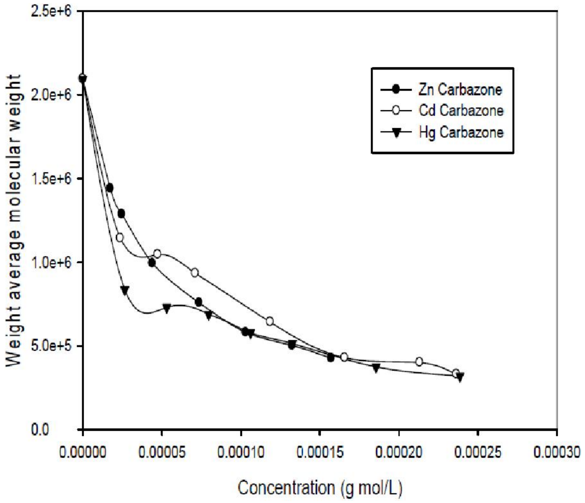


Figure 3 : Effect of metal carbazone complexes concentration on the weight average molecular weight

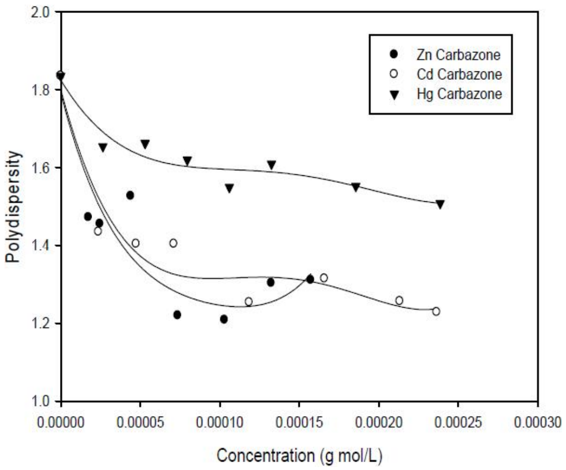


Figure 4 : Effect of metal carbazone complexes concentration on the polydispersity of PMMA

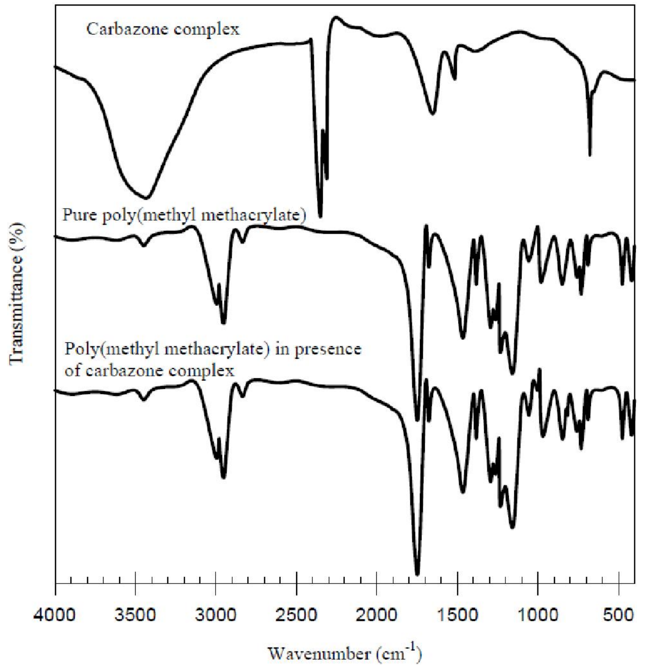


Figure 5 : FT-IR spectra of carbazone complex, pure poly (methyl methacrylate) and poly (methyl methacrylate) in presence of carbazone complex

Polymer structure and crystallinity

The FT-IR spectral chart of carbazone complexes are exhibiting their characteristic absorption bands at 3448, 1642, 1515, and 677 cm^{-1}that are arising from N–H stretching vibration, C=N stretching, N=N stretching, and N–H out of plane bending vibration, respectively and as shown from Figure 5. This is in addition to the doublet band at 2353-2312 cm^{-1} which arising from N=C–N=N moiety[15]. Poly (metyl methacrylate) spectral is also characterized though its the main characteristic FT-IR peaks at 3011, 2949 and 1745 cm^{-1} for isotactic structure which are assigned to υ_a(C–H), υ_s(C–H) and υ(C=O) respectively and at 1456 and 1286 cm^{-1} for syndiotactic structure which are assigned to $\delta_a(\alpha\text{–CH})$, and $\delta_s(\alpha\text{–CH}_3)$ respectively and at 1199 cm^{-1} for the skeletal, Figure 6[16]. When PMMA samples prepared in the presence of carbazone complex are subjected to FT-IR spectroscopy studies, Figure 6 (a-c) was produced. Figure 6 confirms once again the specific structural features of PMMA, in addition to the peaks referred to the complex compound employed such as N–H stretching vibration band at 3448 cm^{-1}, N=N stretching vibration band at 1515 cm^{-1}, N–H out of plane bending vibration band at 677 cm^{-1}, noticing that the disappearance of the doublet band at 2353-2312 cm^{-1} for N=C–N=N in addition to the appearance of two new week bands at 1000 and 820 cm^{-1} which are arising from CH_2–N stretching vibration. Such structural observation could be attributed the homolytic rapture to N=N and N–H bonds of the complex compound by the radical formed in the medium that might lead to the formation of many active centers on the complex compound explaining its ability to work as a cross linking agent.

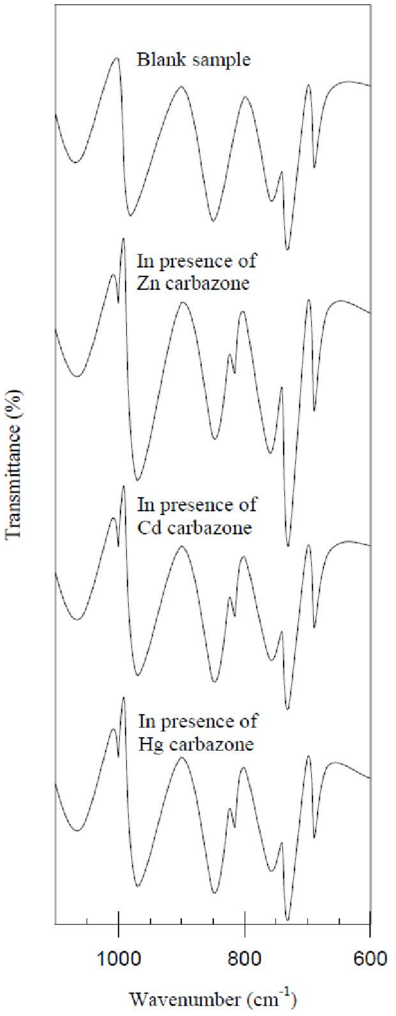


Figure 6 : FT-IR spectra profile of poly (methyl methacrylate) in the absence and presence of different metal carbazone complexes

X-ray examination for all the polymer samples prepared in absence and presence of zinc, cadmium and mercury carbazone complexes at different concentrations is illustrated in Figure 7. The X-ray pattern confirms an improvement of the polymer chains order due to the presence of these complexes whereas three reflexes appear at 2θ = 14, 30 and 42°. While, in case of pure polymer, such reflexes were completely absent when compared to pure poly (methyl methacrylate) which is nearly amorphous[17], Figure 7. Calculated relative degrees of crystallinity[18] of all samples are presented in Figure 8. The results reveal that cadmium and mercury carbazone complexes are of high relative degree of crystallinity at low complex concentrations that decrease as the concentrations increased. On the contrary, in case of zinc carbazone complex the behavior inversed, whereas, the best improvement in the relative degree of crystallinity occur at high concentration. Therefore, it seems reasonable to conclude that there is a direct relationship between metal complex stability and polymer characterization. Whereas, at a high complex concentration, a higher number new active centers are produced during the polymerization process, which will lead definitely to randomness increase and subsequently decreasing the order of the polymeric chain packing[19].

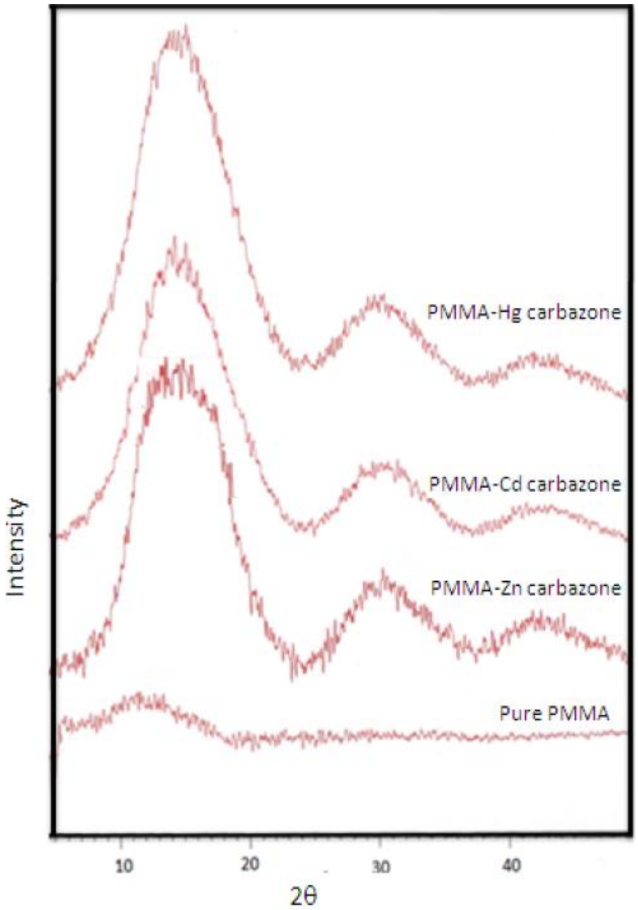


Figure 7 : X-ray diffraction patterns for poly (methyl methacrylate) in the absence and presence of different metal carbazone complexes

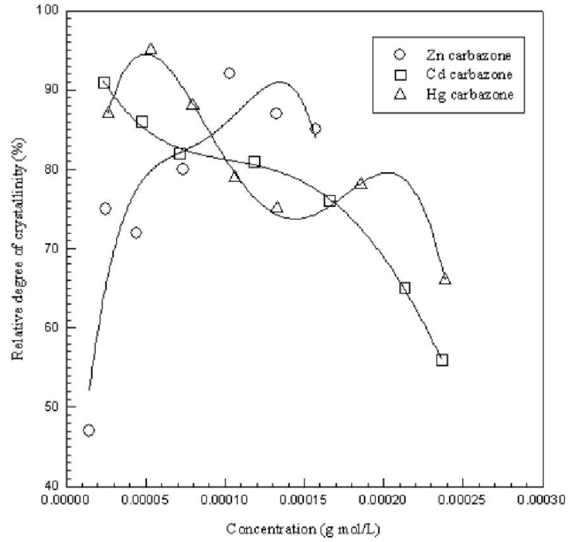
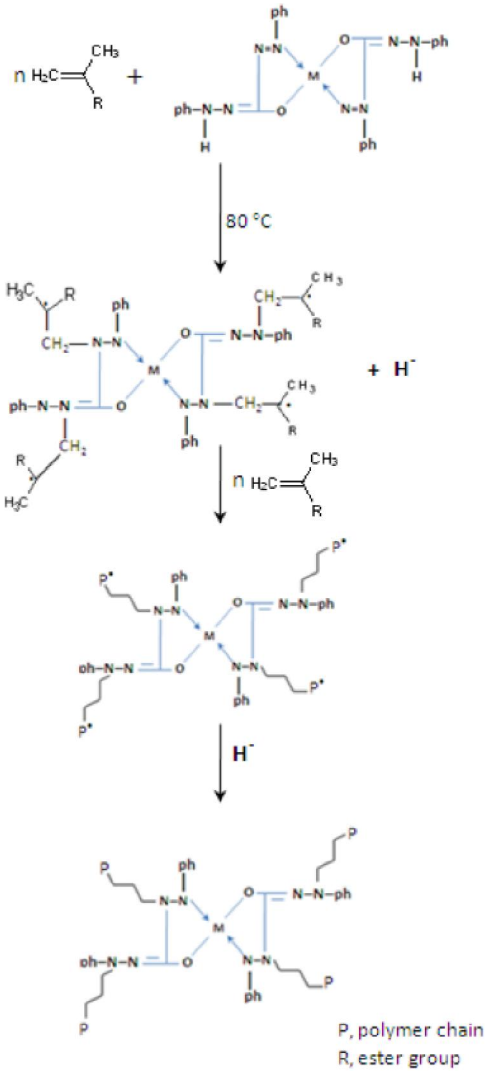


Figure 8 : Effect of metal carbazone complexes concentration on the relative degree of crystallinity



P, polymer chain
R, ester group

Figure 9 : Mechanism for catalytic chain transfer of methyl methacrylate

Pathway of MMA polymerization in presence of carbazones

Polymers molecular weight parameters, FT-IR and x-ray diffraction data usually support reaction mechanism elucidation[20,22]. Accordingly, a suggested mechanism was thought for the polymerization of methyl methacrylate in the presence of metal carbazone relevant to the reaction conditions employed and as illustrated in Figure 9. The proposed MMA polymerization mechanism in presence of carbazone complexes was based on the following observations and facts:

1) The change of color during polymerization process is noticed and is mainly due to changing of the azo form to the hydrazo indicating that these complexes can be used as reliable indicators for the free-radical polymerization.
2) The production of MMA polymers with low molecular weights can be argued as due to the role of the carbazone complexes as a chain transfer agent whereas the growing polymer chain abstracting the H-radical forming a dead polymer.
3) The improvement in the crystallinity for all samples is interpreted on the basis of the formation of excessive active center during the polymerization process due to the presence of the complex compounds. Such conclusion could also lead to the ability of employing such technique complex compounds as across linking agent during highly crystalline (ordered) PMMA.

The above conclusions should encourage more elaborate work in relative fields to add more value to the role of carbazone and dithizone in improving not only the thermal behavior of vinyl polymers but also their direct impact and effect on the stage's order during polymerization.

REFERENCES

[1] N.G.McCrum, C.P.Buckley, C.B.Bucknall; Principles of polymer engineering, 2nd Edition, Oxford Scientific Publications, Oxford, **(1999)**.

[2] A.A.Gridnev, S.D.Ittel; Chem.Rev., **101**, 3611 **(2001)**.

[3] G.T.Russell; Aust.J.Chem., **55**, 399 **(2002)**.

[4] G.Moad, C.L.Moad; Macromolecules, **29**, 7727 **(1996)**.

[5] B.R.Smirnov, V.D.Plotnikov, B.V.Ozerkovskii, V.P.Roshchupkin, N.S.Yenikolopyan; Polym.Sci. USSR, **33**, 2807 **(1981)**.

[6] B.R.Smirnov, A.P.Marchenko, V.D.Plotnikov, A.I.Kuzayev, N.S.Yenikolopyan; Polym.Sci.USSR, **23**, 1169 **(1981)**.

[7] G.P. Abramo, J.R.Norton; Macromolecules, **33**, 2790 **(2000)**.

[8] E.Grognec, J.Claverie, R.Poli; J.Am.Chem.Soc., **123**, 9513 **(2001)**.

[9] M.Walickis, J.Kroh; Acad.Polon.Sci.Ser.Sci. Chem., **13**, 635 **(1965)**.

[10] W.Oelschlager, E.Schwarz; Zh.Anal.Chem., **258**, 203 **(1972)**.

[11] A.Goto, T.Suzuki, H.Ohfuji, M.Tanishima, T.Fukuda, Y.Tsujii, H.Kaji; Macromolecules, **44**, 8709 **(2011)**.

[12] Yu.A.Kabochii, S.Yu.Kochev, P.M.Valetski; Polym.Sci.B, **48**, 32 **(2006)**.

[13] E.V.Chernikova, A.V.Tarasenko, E.S.Garina, V.B.Goluber; Polym.Sci.A, **50**, 353 **(2008)**.

[14] C.Pugh, A.Singh, R.Samuel, K.Ramos; Macromolecules, **43**, 5222 **(2010)**.

[15] B.Stuart; Infrared spectroscopy: Fundamentals and applications, John Wiley & Sons, Ltd, England, **(2004)**.

[16] A.Fawcett; Polymer spectroscopy, John Wiley & Sons, Ltd, England, **(1996)**.

[17] W.Hanna, M.Mekewi, E.El-Mosallamy; J.Appl. Polym.Sci., **82**, 562 **(2001)**.

[18] L.Segal, J.Greely, A.Martin, L.Conrad; Text.Res.J., **29**, 786 **(1959)**.

[19] E.El-Mosallamy; J.Polym.Res., **8**, 253 **(2001)**.

[20] A.Galano, A.Martinez; J.Physical Chemistry, **116**, 1200 **(2012)**.

[21] T.Furuncuglu, I.Ugur, T.Degirmenci, V.Aviyente; Macromolecules, **43**, 1823 **(2010)**.

[22] E.Sadek, M.Mekewi, F.Yehia, S.Solyman, S.Hassan; Macromol.Chem.Phys., **202**, 1505 **(2001)**.