

Thermal Stability Eminence of PMMA Prepared in Presence of Photosynthesized Ruthenium Carbonyl Schiff Base as a Catalyst

Teraze A. Youssef, Mohamed A. Mekewi

Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

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ABSTRACT: Sunlight irradiation reaction of $\text{Ru}_3(\text{CO})_{12}$ with a Schiff base, bis (acetyl acetone) ethylene diimine, acacenH₂, in benzene results in the formation of an octahedral complex $[\text{Ru}(\text{CO})_2(\text{acacen})]$ with a tetradentate ligand. The complex was structurally confirmed using elemental analysis, infrared, mass spectrometry, ¹HNMR, UV-vis absorption spectra, and magnetic measurements. $[\text{Ru}(\text{CO})_2(\text{acacen})]$ complex compound was then used as a catalyst for the polymerization of methyl methacrylate (MMA) in the presence of sodium bisulfite as a cocatalyst. FT-IR, gel permeation chromatography (GPC) was used as a tool for structure confirmation and molecular weights of the poly methyl methacrylate (PMMA). The stability of

the catalyzed polymer against thermal degradation was investigated using thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) to assess its distinctive thermal stability. Higher thermal stability of PMMA samples prepared in presence of $[\text{Ru}(\text{CO})_2(\text{acacen})]$ compared with blank PMMA were clearly observed. A reaction mechanism was suggested based on the coordination of the complex compound with the polymeric chains. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1503–1510, 2009

Key words: ruthenium complexes; Schiff base; PMMA; thermal stability; copolymerization

INTRODUCTION

Schiff base-metal complexes are characterized by interesting and important properties, such as their ability to reversibly binding oxygen in epoxidation reaction,¹ biological activity,^{2–5} complexing ability toward some toxic metals,⁶ catalytic activity in hydrogenation of olefins,⁷ and photochromic properties.^{8,9} Transition metal carbonyls were indicated as reactive during several reactions, where carbon monoxide serves mainly as the provider of reactivity and stability.⁷ Reactions of Group 6 and 8 metal carbonyls with some selected Schiff bases having oxygen and nitrogen donors were investigated.^{10–13} Carbonyl complexes of ruthenium play an important role in homogeneous catalysis.¹⁴ Previous study on the catalytic activity of the synthesized polymer-anchored Ru(III) Schiff base complex was investigated for hydrogenation of styrene and oxidation of benzyl alcohol where higher catalytic activity was found in case of supported catalyst.¹⁵ Accordingly, such claimed reactivity of transition metal carbonyls is promising for the solution polymerization processes. In the

present article, PMMA was prepared in the presence of $[\text{Ru}(\text{CO})_2(\text{acacen})]$ as a catalyst and NaHSO₃ as an initiator at different concentrations of ruthenium acacen complex to develop highly resistance polymers toward thermal degradation atmospheres.

EXPERIMENTAL

Chemicals

$\text{Ru}_3(\text{CO})_{12}$ and methyl methacrylate monomer were supplied by Aldrich. Bis (acetyl acetone) ethylene diimine was prepared as described earlier, Figure 1.¹⁶ All solvents were of analytical reagent grade and were purified by standard methods.

Instrumentation and techniques

IR measurements (KBr pellets) were performed using Unicam-Mattson 1000 FT-IR spectrometer. Electronic absorption spectra were performed using Unicam UV2-300 UV-vis spectrophotometer. NMR measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. The ligand and its complex were dissolved in deuterated DMSO using TMS as internal reference. Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer and mass spectrometry measurement of the complex was performed on a Finnigan MAT SSQ 7000. Thermal stability of the polymer was investigated using

Correspondence to: T. A. Youssef (trease_albert@yahoo.com).

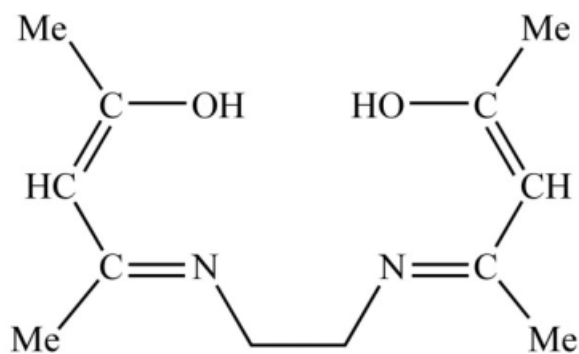


Figure 1 AcacenH₂ ligand.

thermogravimetric analysis (TGA) under nitrogen atmosphere with a heating rate 10°C/min using a Shimadzu DT-50 thermal analyzer. Molecular weight characterization of polymer was performed by using gel permeation chromatography (GPC) technique employing Gligent GPC 1100 Series, Germany, PLb gel 100, 10,000, 10,0000 no. series, and the porosity is 5 μm and refractive index detector.

Synthesis of [Ru(CO)₂(acacen)]

A mixture of [Ru₃(CO)₁₂] (0.10 g, 0.16 mmol), acacenH₂ (0.107 g, 0.48 mmol) and 30 cm³ benzene was placed in a sealed tube, irradiated under sunlight for about 11 h. The solvent was removed on a vacuum line. The residue was washed several times by boiling petroleum ether and then recrystallized from hot THF giving brown crystals. The complex was left to dry in vacuum for several hours, giving a yield of 60%. CHN analysis of C₁₄H₁₈N₂O₄ Ru results in the following: C = 44.1%, H = 4.7%, and N = 7.3% with a mere compatibility to the calculated values of C = 44.3%, H = 4.8%, and N = 7.5%. *M/z* = 379[P-(Ru-CO)]⁺. IR data: ν(C=N), 1605.8 s; ν(C=O), 2048.6 s, 1973.7 s; ν(C=C), 1415 m; ν(C-O), 1281.2 cm⁻¹. ¹HNMR data: 1.94 (s, CH₃); 3.35 (s, CH₂); 4.94 (w, CH).

Solution polymerization procedure

Monomer solution mixture was prepared by mixing the inhibitor free methyl methacrylate (MMA) with dry acetone and 0.05 mL of 0.1 M sodium bisulfite solution (the sodium bisulfite was added for its activity as a reducing agent in addition to its role as a cocatalyst).¹⁷ A stock solution of [Ru(CO)₂(acacen)] complex was prepared by dissolving 0.05 g of the solid complex in 50 mL DMSO. The samples were prepared by mixing 10 mL of the MMA solution with different volumes of ruthenium complex solution (1.1, 2.0, 2.4, 3.0, and 4.0 mL, respectively) in glass ampoules. The glass tubes containing the reaction mixtures were then sealed under the flow of purified dried nitrogen gas and finally placed in an adjusted oven at 80°C for 8 h. After the elapse of time, the

ampoules were opened and the polymer product was dissolved completely in toluene, filtered off carefully several times before is finally cast as a film by allowing the solvent to evaporate completely in vacuum atmosphere at ambient temperature.

RESULTS AND DISCUSSION

Catalyst structure and characterization

IR and NMR studies

The IR of the free ligand, acacenH₂, shows its characteristic bands due to ν_{O,H}, ν_{C=N}, ν_{C=C}, and ν_{C-O} at

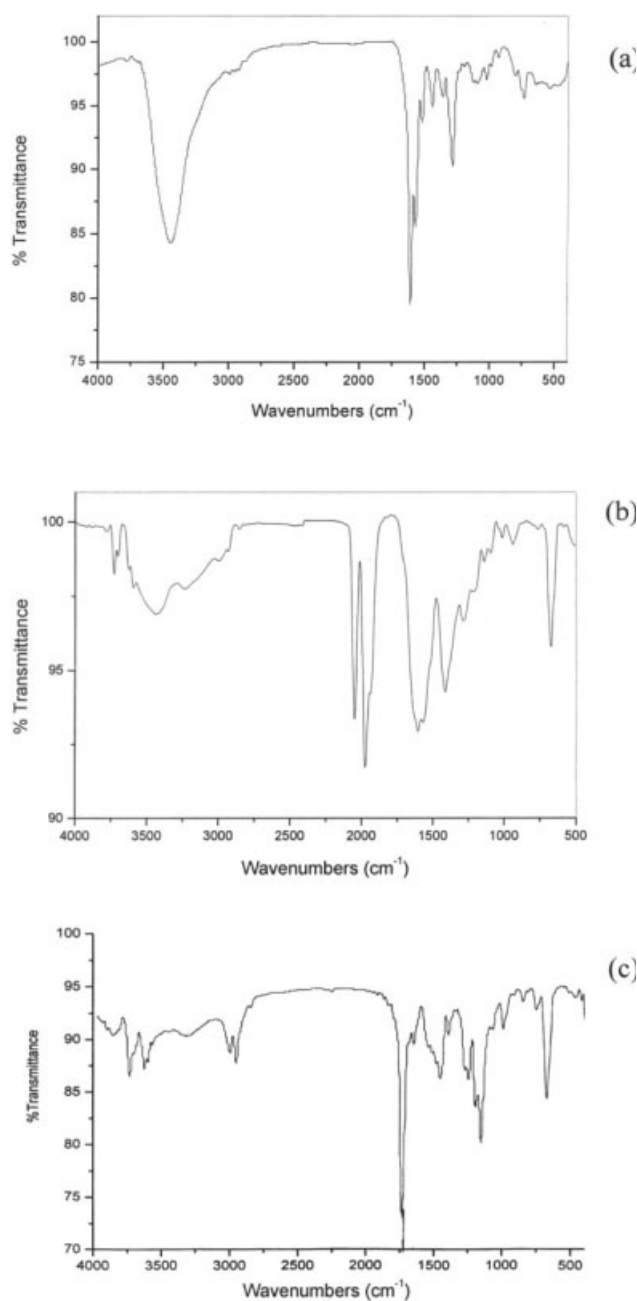


Figure 2 FT-IR spectrum of acacenH₂ (a); [Ru(CO)₂(acacen)] (b); and blank PMMA (c).

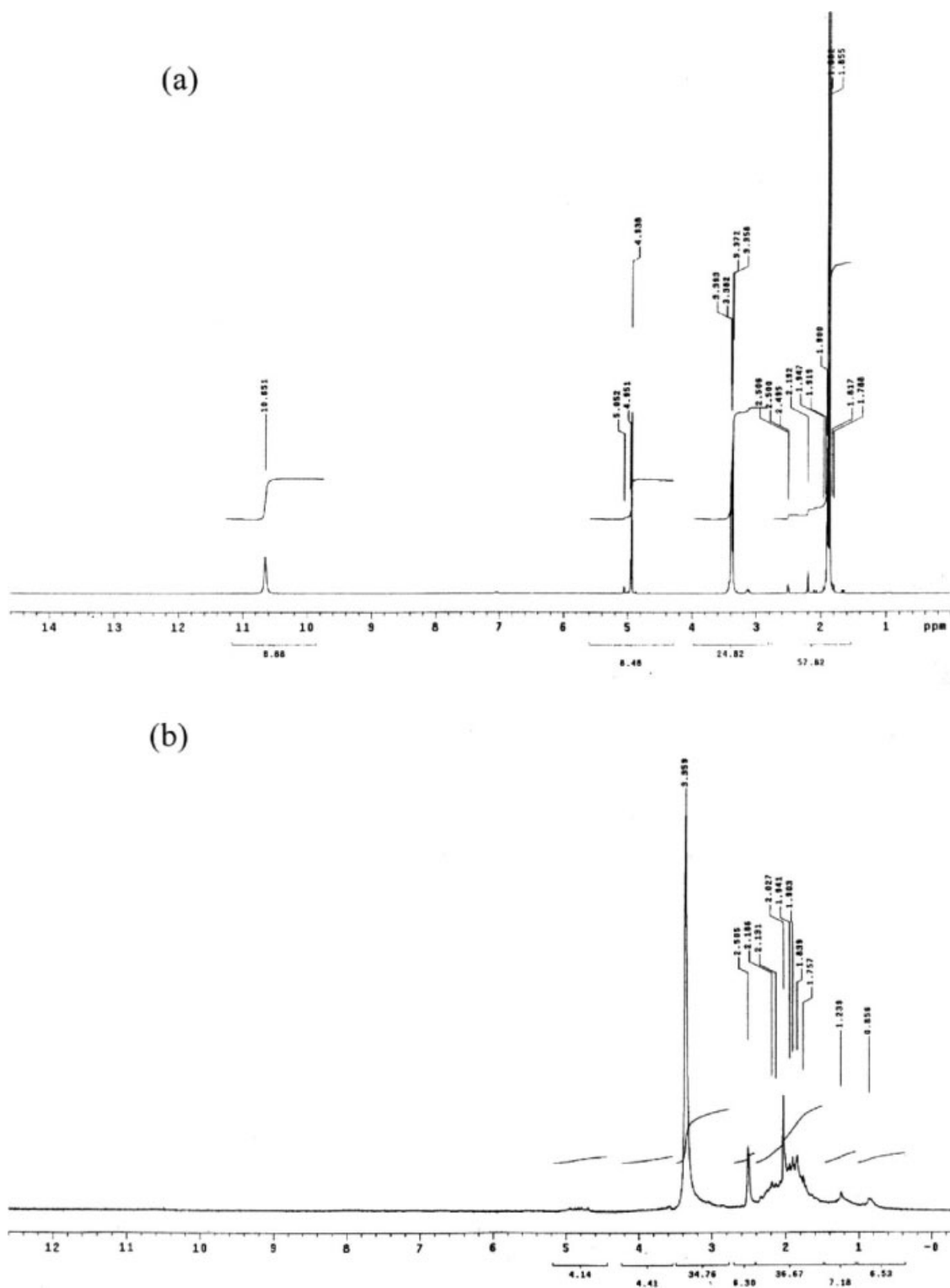


Figure 3 ^1H NMR spectrum of acacenH₂ (a) and [Ru(CO)₂(acacen)] (b).

3443.3, 1608.2, 1440.5, and 1288.8 cm^{-1} , respectively, Figure 2(a). IR spectrum of [Ru(CO)₂(acacen)] complex displayed the characteristic ligand bands with appropriate shifts because of complex formation, Figure 2(b). The spectrum of the complex experienced the disappearance of the ligand band due to ν_{OH} .

Elimination of the hydrogen from the O—H groups, which was confirmed through the disappearance of the OH signal in the ^1H NMR spectrum of the complex indicate the deprotonation of the enolic proton before coordination, Figure 3. Also a band observed at 1288.8 cm^{-1} in the spectrum of free ligand, which

has been assigned to C—O stretching, was shifted to 1281.2 cm^{-1} , indicating the coordination to the metal through the enolic oxygen.^{12,18} Furthermore, coordination of the ligand to the metal through nitrogen atom is expected to reduce the electron density in the azomethine link and lower the $\nu_{\text{C}=\text{N}}$ absorption frequency. The band due to $\nu_{\text{C}=\text{N}}$ showed a negative shift and appeared at 1605.8 cm^{-1} in the IR spectrum of the complex, indicating the coordination of azomethine nitrogen to ruthenium metal.¹² In addition, the IR spectrum of the complex compound exhibited two strong bands in the metal carbonyl region at 2048.6 and 1973.7 cm^{-1} due basically to the symmetric and asymmetric stretching frequencies of two CO groups.¹⁹ This could indicate that the two CO groups are bound *cis*- to each other in a distorted octahedral arrangement. The distortion of the octahedral arrangement may be explained as based on the non-coplanar characteristics of the Schiff base molecule.²⁰ In the far IR spectrum of the complex compound, the nonligand bands observed at 510.7 and 453.7 cm^{-1} due to Ru-O and Ru-N bond giving rather a conclusive evidence for the bonding of azomethine nitrogen and enolic oxygen, i.e., the ligand to the metal ion.^{20,21} Therefore, it can be concluded that acacenH₂ ligand probably coordinated to ruthenium atom through enolic oxygen and azomethine nitrogen and acting as a tetradentate ligand. Magnetic measurement showed that the complex is diamagnetic. According to the proposed structure, the ruthenium has +2 formal oxidation state with d⁶ electronic configuration (Fig. 4). The ¹HNMR spectra of the complex and free ligand in DMSO gave similar pattern except the disappearance of the OH signal in the ¹HNMR spectrum of the complex. The ¹HNMR spectrum of the complex was recorded to confirm the binding of Schiff base to the ruthenium ion. In the spectra, a multiplet was observed in the δ 1.94 ppm region corresponding to the methyl protons of the Schiff base ligand. The methylene proton signal

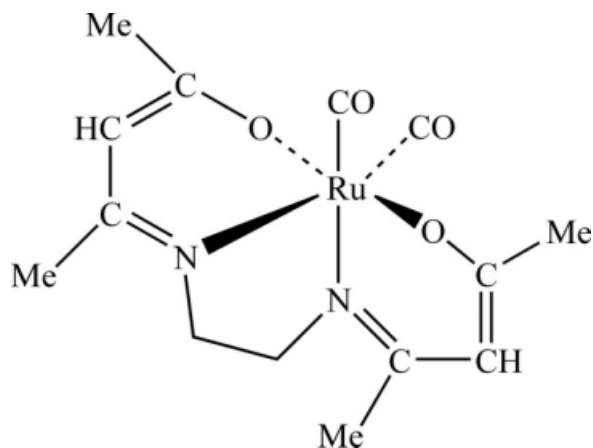


Figure 4 [Ru(CO)₂(acacen)].

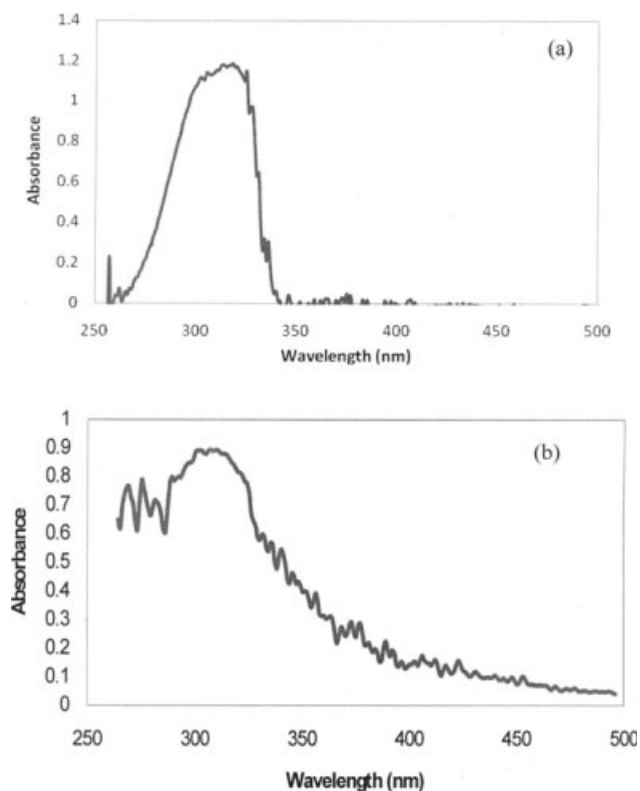


Figure 5 UV-vis spectra of acacenH₂ (a) and [Ru(CO)₂(acacen)](b) in DMSO.

appeared as strong singlet in the δ 3.35 ppm region and the resonance for the methine protons as a singlet in the δ 4.94 ppm region.²²

UV-vis studies

The electronic spectra of the Schiff base and the complex have been measured in DMSO, Figure 5. The ground state of ruthenium (II) in octahedral environment is ¹A_{1g} arising from the t_{2g}⁶ configuration and the excited states corresponding to the t_{2g}⁵eg¹ configuration are ³T_{1g}, ³T_{2g}, ¹T_{1g}, and ¹T_{2g}. Hence, four bands corresponding to the transition ¹A_{1g} → ³T_{1g}, ¹A_{1g} → ³T_{2g}, ¹A_{1g} → ¹T_{1g}, and ¹A_{1g} → ¹T_{2g} are possible in order of increasing energy.²³ The spectrum of the complex showed a band at 375 nm, which has been assigned to the charge transfer transition arising from the excitation of electron from the metal t_{2g} level to the empty molecular orbitals derived from π* level of the ligand.^{24–26} The other high intensity bands in the region 278–333 nm were characterized by ligand-centered (LC) bands and has been designated as π-π* and n-π* transitions for the electrons localized on the azomethine group of the Schiff base.²³ The pattern of the electronic absorption spectrum of the complex indicated the presence of an octahedral environment around ruthenium (II) ion, similar to that of other ruthenium (II) octahedral complexes.^{24,25,27} On the other hand,

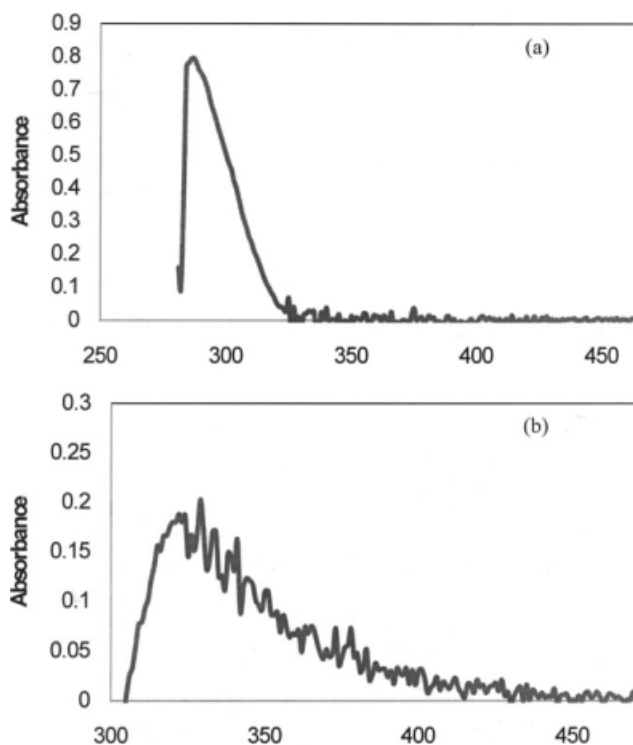


Figure 6 UV-vis spectra of blank PMMA (a) and catalyzed PMMA (b) in toluene.

UV-vis studies for the catalytic polymerized PMMA against native polymer PMMA (blank polymer prepared in the absence of the complex catalyst) in toluene showed absorption band at 333 nm, which could indicate the higher stability of the ligand-centered (LC) bands, Figure 6.

PMMA structure and characterization

Polymer structural aspects

The FT-IR analysis for native PMMA in Figure 2(b) and catalyzed PMMA are illustrated in Figure 7. The FT-IR spectra show typical absorption peaks for the PMMA as reported earlier.^{28–30} As could be observed from the FT-IR chart, the complex compound seems to have influenced the polymer distinguished peaks with new absorption peaks, which is not observed

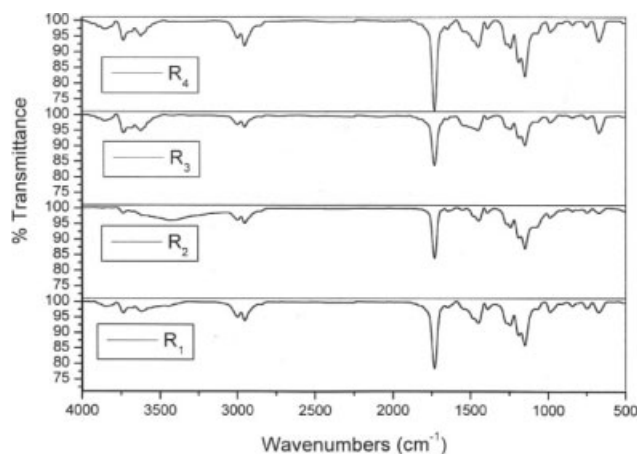


Figure 7 FT-IR spectrum of catalyzed PMMA samples.

with the native PMMA. Such result indicates clearly the involvement of the catalyst complex molecules into coordinated macroradical species. The disappearance of the characteristic carbonyl bands of the complex at 2048.6 and 1973.7 cm^{-1} was also observed, which indicates a possible role for the carbonyl groups as the source of reactivity increasing metal electron density to coordinate with monomer radicals as reported earlier.³¹ Such coordination is clearly evidenced from the appearance of the indicative Ru complex bands at 1605.8, 1566.4, 1432.5, 1281.2, 510.7, and 453.7 cm^{-1} , for the catalyzed PMMA with a slight shift due to imminent coordination between the macroradical and Ru complex compound species.

Polymer conversion % and catalyst selectivity

Catalytic polymerization of MMA using ruthenium (II) acacen complex compound was performed as described earlier and the results of conversion %, molecular weight parameters, and polydispersity are illustrated in Table I. Polymer molecular weight parameters of number average molecular weight (M_n) and weight average molecular weight (M_w) determined using GPC technique revealed that at catalyst concentration of 2.90×10^{-3} mmol, conversion % of 60.9 is obtained at respective M_n of 32,906

TABLE I
Conversion %, Molecular Weight Parameters and Polydispersity Related to Blank PMMA and Catalyzed PMMA at Different Concentrations

Sample	Catalyst Concentration $\text{mmol} \times 10^{-3}$	Conversion, %	$M_n \times 10^4$	$M_w \times 10^5$	PD ^a
Blank	0	12.5	20.6241	4.33557	2.10
R ₁	2.90	60.9	3.2906	1.2764	3.88
R ₂	5.28	47.4	2.9000	1.1024	4.00
R ₃	6.33	53.2	2.4710	1.0067	4.07
R ₄	7.92	30.1	1.4020	2.5220	4.18
R ₅	10.05	10.4	6.9363	2.9549	4.24

^a PD (polydispersity) = M_w/M_n .

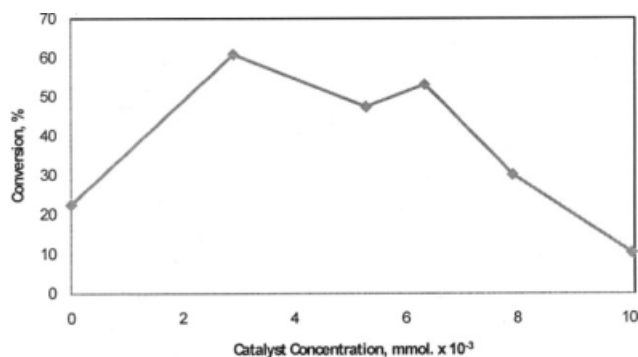


Figure 8 Relation between catalyst concentration and conversion %.

and M_w of 127,640, with a polydispersity value of 3.8. Figure 8 illustrates the PMMA conversion dependence on the catalyst concentrations where polymer conversion % increased to a maximum of 60.9% as catalyst concentration decreased to 2.9×10^{-3} mmol. Figure 9 represents the profile of the dependence of M_w on the catalyst concentration where a continuous drop of M_w to a minimal value of 1×10^5 is observed as catalyst concentration increases to 6.3×10^{-3} mmol, then moderately increases to 2.9×10^5 with further increase of catalyst concentration. Figure 10 illustrates the relationship between molecular weight parameters (M_w and M_n) and the conversion %. As observed, almost the same pattern of dependence is revealed for both M_w and M_n , indicating polydispersity consistency for samples prepared at different concentrations. From the results of the polymerization reaction it seems that the available complex compound oxidation states act as a radical transfer propagating step analogue to general trend adopted by controlled radical polymerization^{32–35} in the presence of an initiator, such as NaHSO_3 , where in its absence such role diminishes. In general, the conversion of MMA to PMMA was found to decrease from 61 to 10% as catalyst concentration increases with a direct impact on the polydispersity toward higher values. Accordingly, a most likely polymerization mechanism is suggested as in Figure 11.

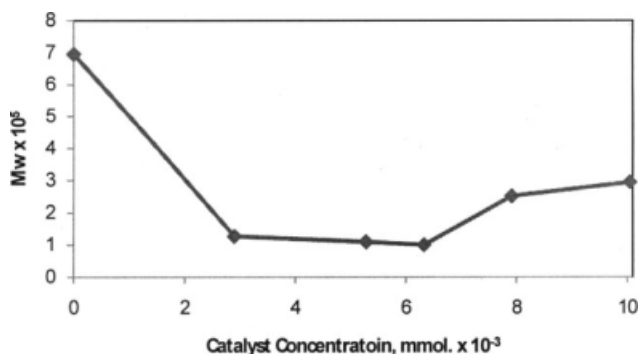


Figure 9 Relation between catalyst concentration and M_w .

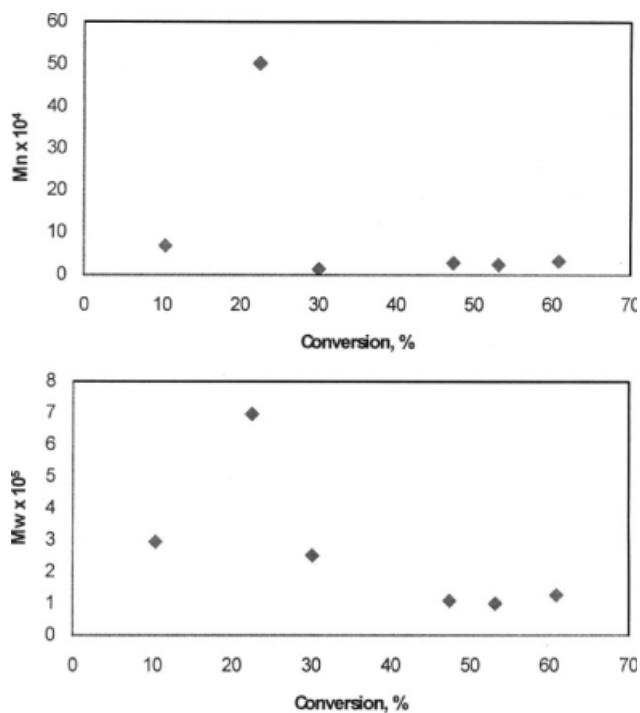


Figure 10 Relation between molecular parameters and conversion, %.

Such mechanism is most favored as depicted from the polymerization results and quite close to what has been reported earlier.^{34–36}

Thermal stability of PMMA

The native PMMA and catalyzed PMMA prepared at different Ru complex concentrations and were subjected to heat up to 600°C using TGA technique. Thermal stability studies through the TGA and DTA follow-up as illustrated in Table II which indicate

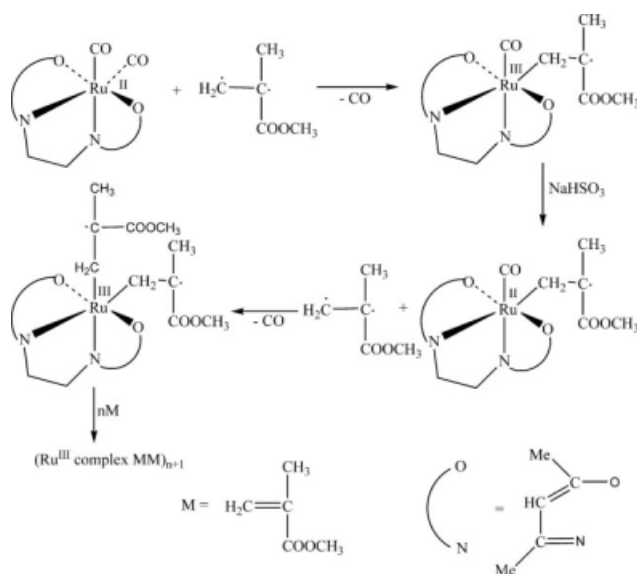
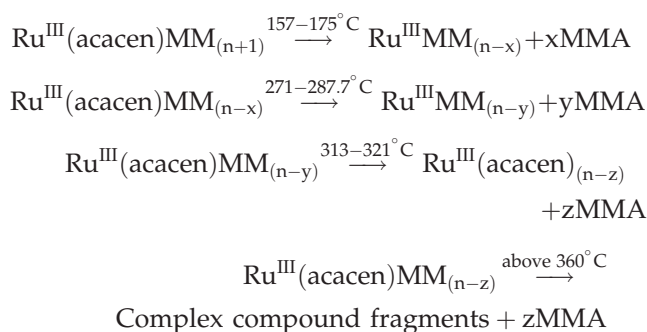


Figure 11 Mechanistic steps of MMA polymerization in the presence of $[\text{Ru}(\text{CO})_2(\text{acacen})]$ as a catalyst.

TABLE II
TGA Data for Blank PMMA and Catalyzed PMMA Samples

Sample	1st Stage temp, °C (% wt loss)	2nd Stage temp, °C (% wt loss)	3rd Stage temp, °C (% wt loss)	4th Stage temp, °C (% wt loss)
Blank	191.8 (10.31)	272.1 (3.46)	340.5 (83.23)	–
R ₁	157.5 (12.86)	287.4 (10.59)	313.4 (15.52)	376.8 (59.19)
R ₂	175.5 (7.43)	277.1 (6.40)	310.2 (27.71)	370.6 (60.97)
R ₃	155.9 (10.84)	268.2 (8.63)	304.2 (25.90)	363.4 (53.55)
R ₄	166.0 (10.00)	273.0 (8.44)	314.0 (18.56)	370.0 (63.00)
R ₅	167.01 (8.11)	271.5 (6.18)	321.9 (15.91)	374.8 (68.95)

- All PMMA catalyzed samples reveal four stages of degradation compared with the blank PMMA prepared in the absence of Ru complex.
- The four-stage degradation phenomenon exhibited degradation ratio and weight loss relative to the catalyst concentration impeded.
- The thermal degradation at lower temperature below 360°C, at all ruthenium complex concentrations, are at a mere 40% weight loss, which could be attributed to a possible energy consumption due to detachment of the complex molecules from the polymeric chains, whereas that at higher temperature than 360°C could be attributed to the polymeric chains backbone secessions as reported by Patnaik³⁷ as well as due to fragmentation of the Ru complex compound.
- At high ruthenium complex concentration of 10×10^{-3} mmol, only 10% conversion was observed, which could be due to the increase of formation of Ru complex compound anhydride ring structure³⁸ which could in turn act as a possible inhibitor instead as a catalyst. This is supported by the increased polymer chains polydispersity values and the decrease observed in the M_n values, Table I.
- As all PMMA samples prepared in presence of different ruthenium complex concentrations, as a catalyst, show degradation to occur up to 360°C with distinguished stepwise degradation at the range of temperatures observed, a mechanism of degradation could then be suggested to occur as follow:



which imply in general that the polymer formed at specific reaction conditions characterized by M_n and M_w values is when subjected to heat suffers

stepwise degradation according to the quantitative release of PMMA fraction at each step.

Such mechanism seems quite convincing mainly based on the facts of the dependence of conversion %, M_n , M_w , and polydispersity values on catalyst concentration and relative thermal degradation profile and McNeill's³⁸ fractional condensation findings of identifying products obtained at thermally degradable stages.

CONCLUSION

The divalent ruthenium complex, $[\text{Ru}(\text{CO})_2(\text{acacen})]$, was isolated from the reaction $\text{Ru}_3(\text{CO})_{12}$ with acacenH₂ ligand in benzene with sunlight irradiation. From the spectroscopic and elemental analysis data, it can be concluded that divalent ruthenium exists in an octahedral environment with acacenH₂ ligand coordinated as a tetradentate with N₂O₂ donor sets. Polymerization of MMA in the presence of Ru(II)acacen complex and sodium bisulfite, as initiator, at different concentrations confirmed the role of the catalyst complex as an active catalyst through a suggested radical propagation polymerization process. The polymer product exhibited thermal stability at a mere 35°C higher than that of the pure polymer PMMA (prepared in absence of Ru(II) acacen complex). Such increased thermal stability could be explained as due to the formation of a coordinated polymer/Ru(II) complex compound, which acts as newly built unit characterized by deviant structural polymer able to elevate its tendency toward thermal degradation. Such findings are supported by structural and molecular weight studies investigations aided by a probable reaction path.

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