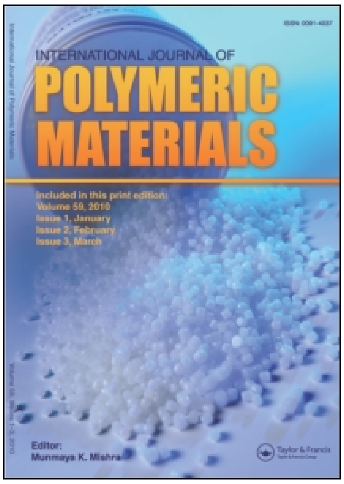

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Salen Transition Metal Complexes as Catalysts for the Synthesis of Photostable Poly(methylmethacrylate)

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To cite this Article Mekewi, Mohamed A.(2005) 'Salen Transition Metal Complexes as Catalysts for the Synthesis of Photostable Poly(methylmethacrylate)', International Journal of Polymeric Materials, 55: 4, 219 — 234

To link to this Article: DOI: 10.1080/009140390927286

URL: http://dx.doi.org/10.1080/009140390927286

International Journal of Polymeric Materials, 55:219–234, 2006

ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/009140390927286

Salen Transition Metal Complexes as Catalysts for the Synthesis of Photostable Poly(methylmethacrylate)

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Polymethylmethacrylate (PMMA) was prepared in presence of Cr (III) and Ni (II) Salen complex compounds as catalysts for the controlled radical polymerization of the methylmethacrylate monomer. The PMMA structure was examined through FT-IR analysis in which characteristic bands of structural tacticity were observed. The PMMA order of tacticity was also identified using ^{1}*HNMR where clear indications of increased polymer tacticity and metal complex intervention with the PMMA growing chains were identified. PMMA samples, prepared in presence of Ni (II) and Cr (III) Salen complex compound, were subjected to various doses of UV light and significant resistance to degradation was noticed. The weight average molecular weight values, using GPC technique, were monitored as the measuring parameter for the PMMA photostability. The results of the present work strongly recommend the use of transition metal Salen complexes as promising catalysts for polymerization of PMMA due to their characteristic activity and the sound resistance toward UV photodegradation the polymer exhibited.*

Keywords: controlled radical polymerization, Ni and Cr Salen complexes, PMMA, photostability, UV

INTRODUCTION

Many transition metal complexes catalysts were reported as useful mediating radical polymerization initiators through specific efficiency parameters and prerequisites [1–6]. Metal complex compounds also proved feasible in bulk, solution, and heterogeneous systems and even during grafting of some natural fibers [7–11]. In such systems, the rate of polymerization is usually governed conditionally and kinetically as reported [12–13], affecting the polydispersity of the final polymer and

Received 22 December 2004; in final form 30 December 2004.

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the mode of loss of end groups [14], for mainly refining the polymer specific properties toward more challenging applications. Among a promising transition metal complex as catalysts are the Salen complexes (Schiff base derivatives derived from the interaction of ethylenediamine and salicyladehyde), which were reviewed so far only for the oligomerization and polymerization of ethylene and propylene and epoxidation of olefins [15–21]. Transition metal complex compounds have also been reported to assist against photodecomposition of the macroradicals and scission of $-CH_2-$ groups [22–23] endowing the polymeric chains with resistance toward photodegradation.

In the present work, Ni (II) and Cr (III) Salen complexes were utilized for the first time as catalysts for the controlled radical polymerization of methylmethacrylate. Suitability and functionality of both complexes are evaluated at a concentration range of 100 to 600 ppm. The catalyst role and direct impact on the conversion yield, variation of structural tacticity of the polymer, and polydipersity parameter, are reviewed. PMMA samples prepared using the aforementioned metal complexes were subjected to various doses of UV radiation and their stability against photodegradation is also evaluated.

EXPERIMENTAL

Chemicals

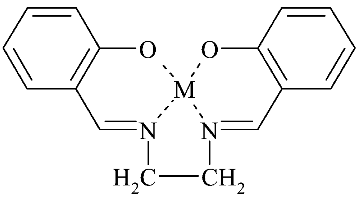
Methylmethacrylate monomer (MMA), transition metal salts, and diamines were all of Aldrich make. Toluene, ethanol, petroleum ether, methanol, acetone, are A.R. grade. All solvents and monomer purity were checked through refractive index measurements using ABBEE II Digital refractometer. All other chemical used were supplied by ADWIC (Egypt).

Ni (II) and Cr (III) Salen Complex Compounds

(Salen) Ethylenediamine Salicyladehyde complexes of Ni (II) and Cr (III) were prepared according to confirmed procedure as stable 3-ring structure, as shown in Scheme 1 [18,24] where M is the metal. The Ni (II) and Cr (III) Salen catalysts were structurally confirmed through ^{1}HNMR analysis after preparation but prior to use.

Polymerization Process

The polymerization of all samples was carried out by first preparing one liter of the monomer solution mixture by mixing a 3:1 ratio of



SCHEME 1

inhibitor free-monomer (MMA) to dry acetone in addition to 1 cc of 0.5 molar of sodium bisulfite solution (the sodium bisulfite has been considered due to its activity as a reducing agent in addition to its role as a co-catalyst) [25].

In a clean glass tube, 20 cc of the MMA solution mixture were added to 10 cc of the Ni (II) and Cr (III) Salen complex solution in dry acetone, corresponding to the total mixture. The glass tube containing the reaction mixture was then sealed under purified dried nitrogen gas and finally placed in an adjusted oven at 80°C for 8 h. After this time period, the ampoules were opened and the polymer product was dissolved completely in toluene, filtered carefully several times before finally being cast as a film by allowing the solvent to evaporate completely in vacuum at ambient temperature.

Conversion Yield and Structural Studies

The conversion yield percent by weight was calculated for all samples prepared in presence of both catalysts at concentration range from 100 to 600 ppm. The structural characteristics of the polymer were studied through FT-IR (ATI Mattson Genesis series FTIR, model 9423-240-08051 with 1001 Fourier drive connected to HR Aldrich polymers library, 2000 Nicollet Instrument Corporation). ^{1}HNMR studies and molecular weight characterization were performed using GPC as reported earlier [7]. Photodegradation studies were carried out at the Photoenergy Center, Ain-Shams University, Cairo, using SUNTEST XLS reactor (Germany) as the source of ultraviolet (UV) radiation. The UV system has been especially designed for the Photoenergy Center to perform materials degradation and stability tests.

RESULTS AND DISCUSSION

Conversion Yield % and Molecular Weight Aspects

The Ni (II) and Cr (III) catalytic activity data with regard to the conversion yield percent of the MMA monomer to the PMMA, the weight

TABLE 1 PMMA Conversion Yield Percent Using Ni (II) and Cr (III) Salen Complex Compounds as Catalysts at Concentration Range of 100 to 600 ppm for 8 h at 80°C

Catalyst concentration, ppm	Conversion yield %		Ni (II) Salen		Cr (III) Salen		Polydispersity	
	Ni (II) Salen	Cr (III) Salen	M_w	M_n	M_w	M_n	Ni (II) Salen	Cr (III) Salen
100	20	58.8	852469	452238	780630	—	1.885	—
200	28	76.5	985650	768837	880020	679552	1.282	1.295
300	32	64	1,552,469	854883	767550	534687	1.816	1.342
400	69	70	3,042,627	2,037928	1,021,988	736219	1.493	1.388
500	20	68	870550	637765	1,210,875	871760	1.365	1.389
600	15	70	575465	411340	865620	607452	1.399	1.395

Blank native PMMA at zero catalyst concentration was found to be of the following values: $M_w = 433557$, $M_n = 206241$, and polydispersirty = 2.10.

average molecular weight, number average molecular weight, and the polydispersity parameter of various samples are illustrated in Table 1. Figure 1 illustrates the dependence of the conversion yield of the PMMA on the concentration of Ni (II) and Cr (III) Salen complexes showing a maximum conversion of 69% in the case of Ni (II) Salen at concentration of 400 ppm and 79% for the Cr (III) Salen at concentration of 200 ppm. In general, Cr (III) Salen complex seemed more active than Ni (II) Salen complex with regard to conversion yields of the PMMA climbing steadily from 58 to 76%. The Ni (II) Salen

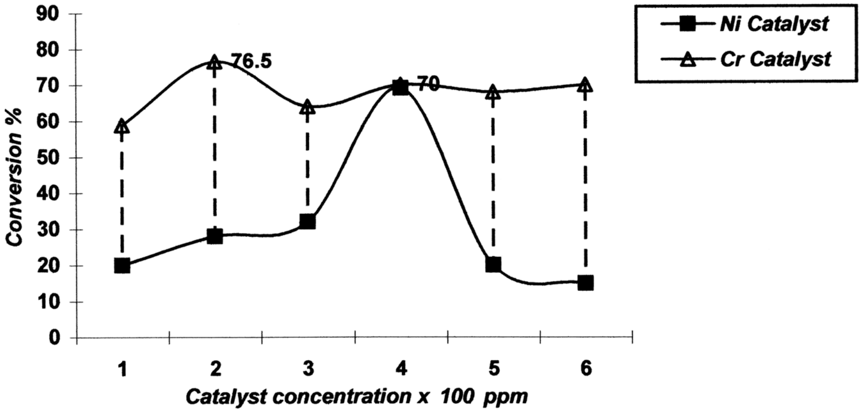


FIGURE 1 PMMA conversion yield % vs. catalyst concentration in ppm of Nickel (II) and Cr (III) Salen complex compounds.

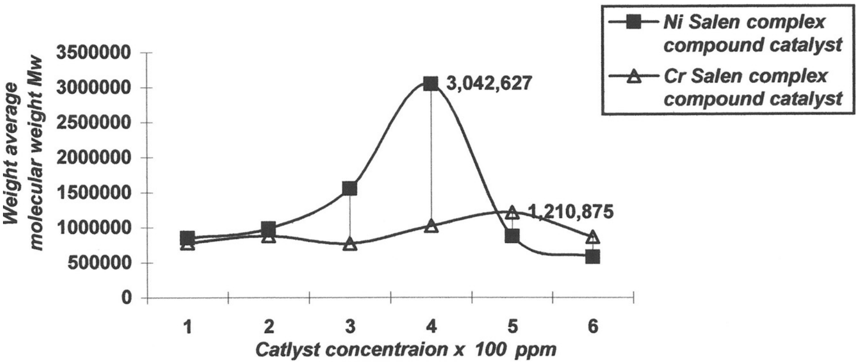


FIGURE 2 Weight average molecular weight values and type of catalyst.

complex compound seem to have achieved the highest weight average molecular weight (M_w) of 3,042,627 at its highest conversion yield of 69% at 400 ppm, whereas at lower and higher concentrations the conversion yield seem to range only between 15 and 32% with an appreciable difference when compared with those exhibited by the Cr (III) Salen concentration (Figure 1). Cr (III) catalyst concentration exhibited the highest M_w of 1,021,988 and 1,210,875 at concentration at 400 ppm and 500 ppm, respectively, at still higher values of conversion yield % (Figure 2). In contrast, the Cr (III) Salen complex catalyst seem to perform consistently with regard to the polydispersity at all catalyst concentrations, ranging from 1.295 at concentration of 200 ppm increasing slightly to a maximum of 1.395 at 600 ppm. In case of Ni (II) Salen complex catalyst, the polydispersity seems to have

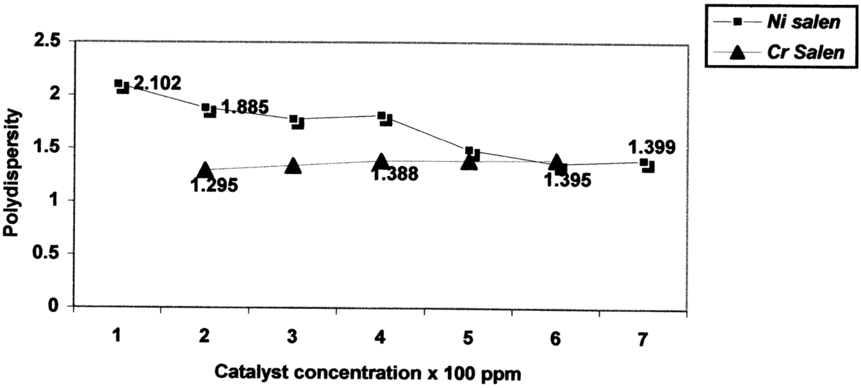
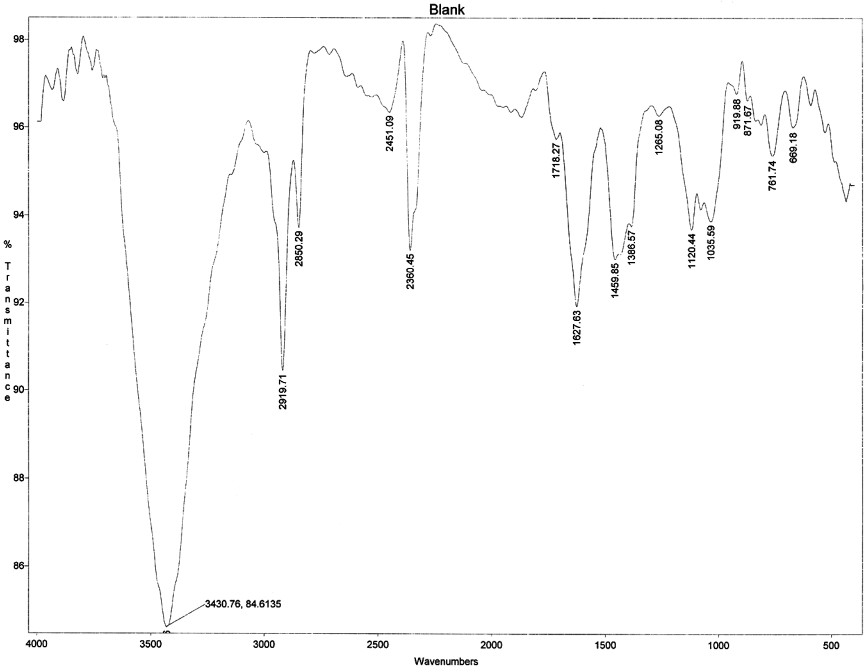


FIGURE 3 Polydispersity variation with catalyst type and concentration.



(a)

FIGURE 4 FT-IR spectra chart of: (a) Blank native PMMA; (b) Ni (II) Salen complex compound; and (c) Cr (III) Salen complex compound.

exceeded 2 and lowers as the catalyst concentration increases with its best value of 1.395 at 600 ppm (Figure 3). The polydispersity results exhibited by Ni (II) and Cr (III) Salen complex compounds indicate an expected material superiority at polydispersity value of 1.395 compared to that prepared in their absences. This dissimilarity in both activity parameters (conversion yield % and polydispersity parameter) that associated with Ni (II) and Cr (III) can be explained as due to corresponding metal stability at various oxidation states. The higher stability of Cr (III) than that of Ni (II) complex compound possibly will favor the increase in the M_w exhibited by the Ni (II) Salen whereas the increase in the conversion yield in case of Cr (III) Salen comes as the result of the many oxidation states Chromium can exhibit once activated through free radicals, thermally occurring in the medium at 80°C, and the higher population in turn of the active centers leading finally to lower molecular weight chains with higher conversion ratios.

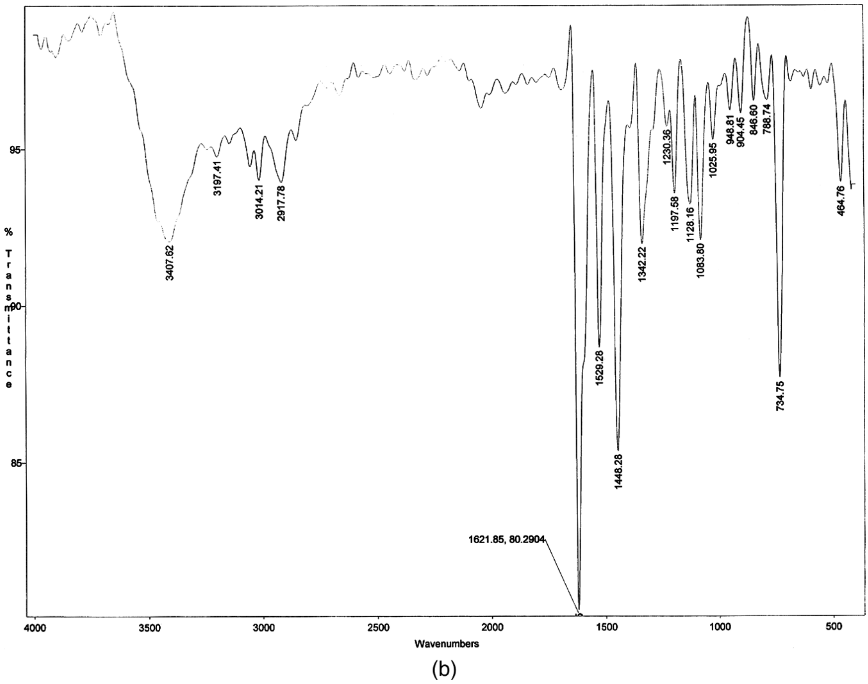
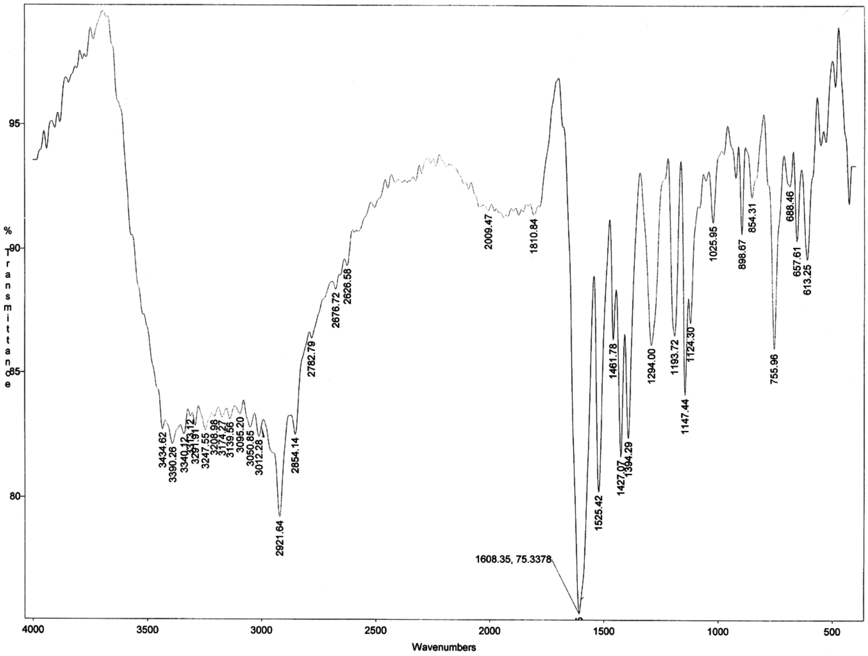


FIGURE 4 Continued.

Mechanistically, it is suggested that the complex compound molecules do interact with thermally activated monomer molecules, leading to a polymeric macroradical through a coordination mechanism. Such interaction might be assisted by subsequent availability of electron delocalization of the ligand structure that could create new sites of active centers on either the ring or on the C=O, according to availability and abundance. Such interaction is evident from the FT-IR and ^{1}HNMR results presented in what follows.

Structural Aspects

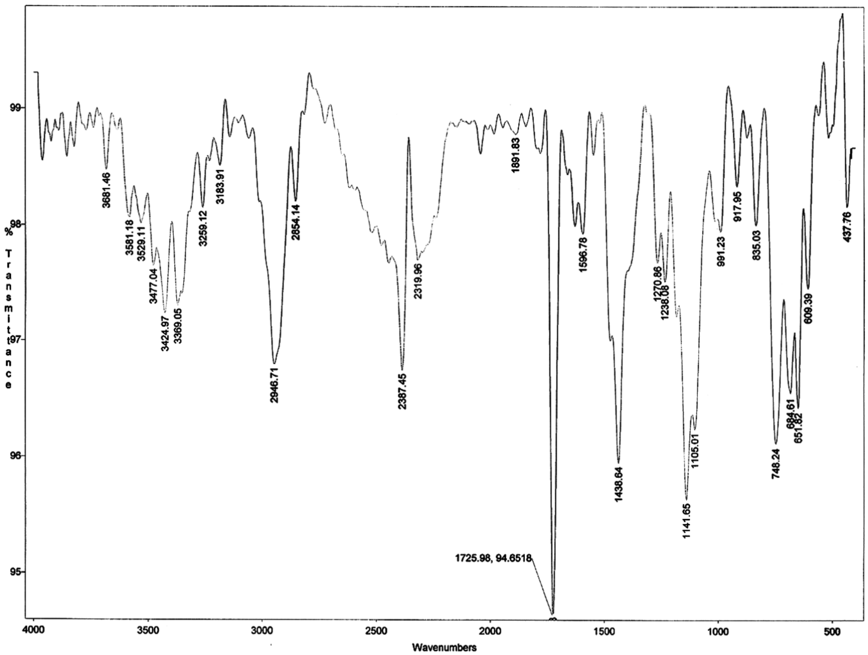
The FT-IR spectra of native PMMA and Ni (II) and Cr (III) Salen complex compounds are shown in Figure 4(a–c) with typical absorption peaks as reported [18,24,26]. PMMA samples prepared in presence of various catalyst concentrations were screened, with results confirming the general absorption spectra of PMMA but with apparent differences due to catalyst intervention and PMMA structural variations. Figure 5(a and b) illustrate the FT-IR absorption spectra of PMMA



(c)

FIGURE 4 Continued.

prepared in presence of 400 ppm Ni (II) and Cr (III) Salen complexes, respectively. As could be observed from the FT-IR chart, both complex compounds seem to have influenced the polymer characteristic peaks with new absorption peaks at 991.23 cm^{-1} and 985.45 cm^{-1}, which are not observed in the native PMMA. The appearance of many new absorption bands indicates clearly the involvement of the catalyst complex molecules in coordinated macroradical species. C–H stretching vibration due to different stretching vibrations of the two-methyl groups associated with the Ni (II) complex are also observed at absorption bands of 2946.71 cm^{-1} and 2952.5 cm^{-1}, Figure 5a. Those at 2850.29 cm^{-1} for the blank PMMA and that at 2854.14 cm^{-1} for PMMA in presence of Ni (II) and 2854.14 cm^{-1} Cr (III), Figure 5b, refer to the methyl group attached to a carbon atom [26]. The deformation of the C–H of the PMMA prepared in presence of Ni (II) Salen complex compound appears at 1444.43 cm^{-1} and at 1386.57 cm^{-1} for the Cr (III). Such deformation indicates that the PMMA samples prepared in presence of Ni (II) and Cr (III) Salen complex compounds have acquired more ordered structure due to the integral involvement of the complex



(a)

FIGURE 5 FT-IR spectra chart of (a) PMMA prepared in presence of 400 ppm Ni (II) Salen complex compound and (b) PMMA prepared in presence of 400 ppm Cr (III) Salen complex compound.

compound in the polymer product, changing its tacticity on one hand and could subsequently induce material physical properties alterations on the other.

^{1}HNMR analyses of the PMMA prepared in the absence or presence of the Ni (II) and Cr (III) Salen complex compounds are illustrated in Figure 6. The native PMMA prepared in absence of the Salen catalyst exhibited typical PMMA resonance proportion of forms of tacticity as shown in Figure 6a. The PMMA prepared in presence of 400 ppm exhibit an increased order toward syndiotatic forms indicating a controlled radical polymerization mechanism [27]. The clear indication of the metal complex intervention with the PMMA is also confirmed by the appearance of a multiplet signal at $\delta = 7.166$ in case of the Cr (III) Salen, and $\delta = 7.160$, 7.225, and 7.248 for Ni (II) salen, which could be due to the phenyl ring protons, and the characteristic methylene proton spectrum at 1.866 for Cr (III), slightly shifted to 1.884 as exhibited by the blank and Ni (II) PMMA samples; see Figure 6(a and b).

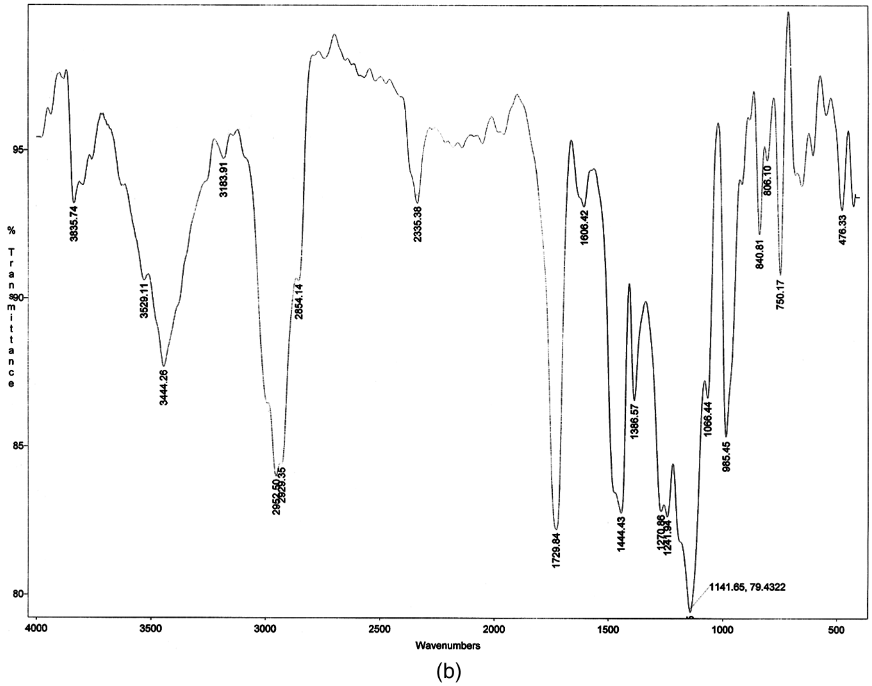
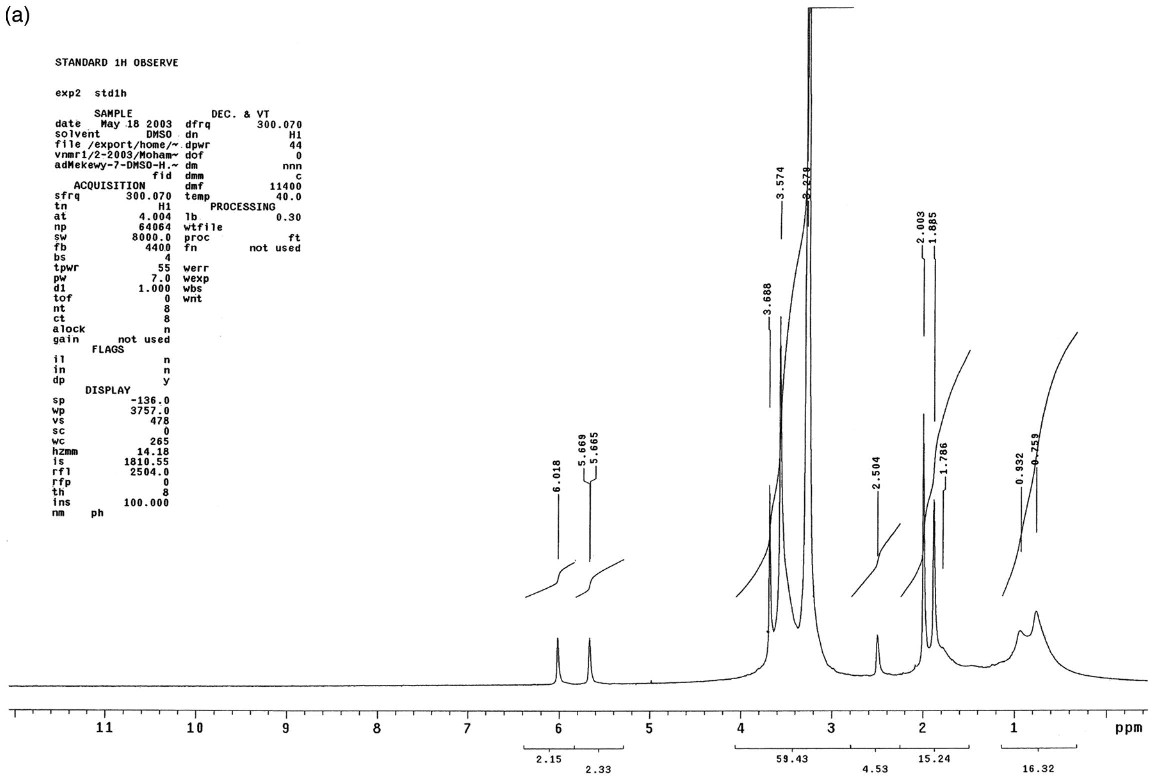


FIGURE 5 Continued.

The aforementioned facts could assist in confirming the postulation of double bond delocalization that is enhanced due to its attachment to the phenyl ring as similarly suggested by Sayyah et al. [28]. In general, both PMMA prepared in presence of the Ni (II) and Cr (III) Salen complexes can be described as of distinguished syndiotactic structure due to the structural interaction of both Ni (II) and Cr (III) Salen complex molecules.

UV Light and Degradation

All samples prepared by using Ni (II) Salen and Cr (III) Salen complex compounds as catalysts for the polymerization at various catalyst concentrations were subjected to various doses of the UV light. The average weight molecular weight reduction was taken as the proven parameter of degradation. Table 2 represent the results obtained with relation to exposure dose. As can be observed, the PMMA prepared in the absence of Salen complex compounds did actually degrade



```
STANDARD 1H OBSERVE

exp2  std1h

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date   May 18 2003  dfrq        300.070
solvent        DMSO  dn               H1
file /export/home/~  dpwr             44
vnmr1/2-2003/Moham~  dof               0
adMekewy-7-DMSO-H.~  dm              nnn
                fid  dmm               c
   ACQUISITION       dmf           11400
sfrq        300.070  temp           40.0
tn               H1     PROCESSING
at            4.004  lb             0.30
np            64064  wtfile
sw           8000.0  proc             ft
fb             4400  fn         not used
bs                4
tpwr             55  werr
pw              7.0  wexp
d1            1.000  wbs
tof               0  wnt
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -136.0
wp           3757.0
vs              478
sc                0
wc              265
hzmm          14.18
is          1810.55
rfl          2504.0
rfp               0
th                8
ins         100.000
nm    ph
```
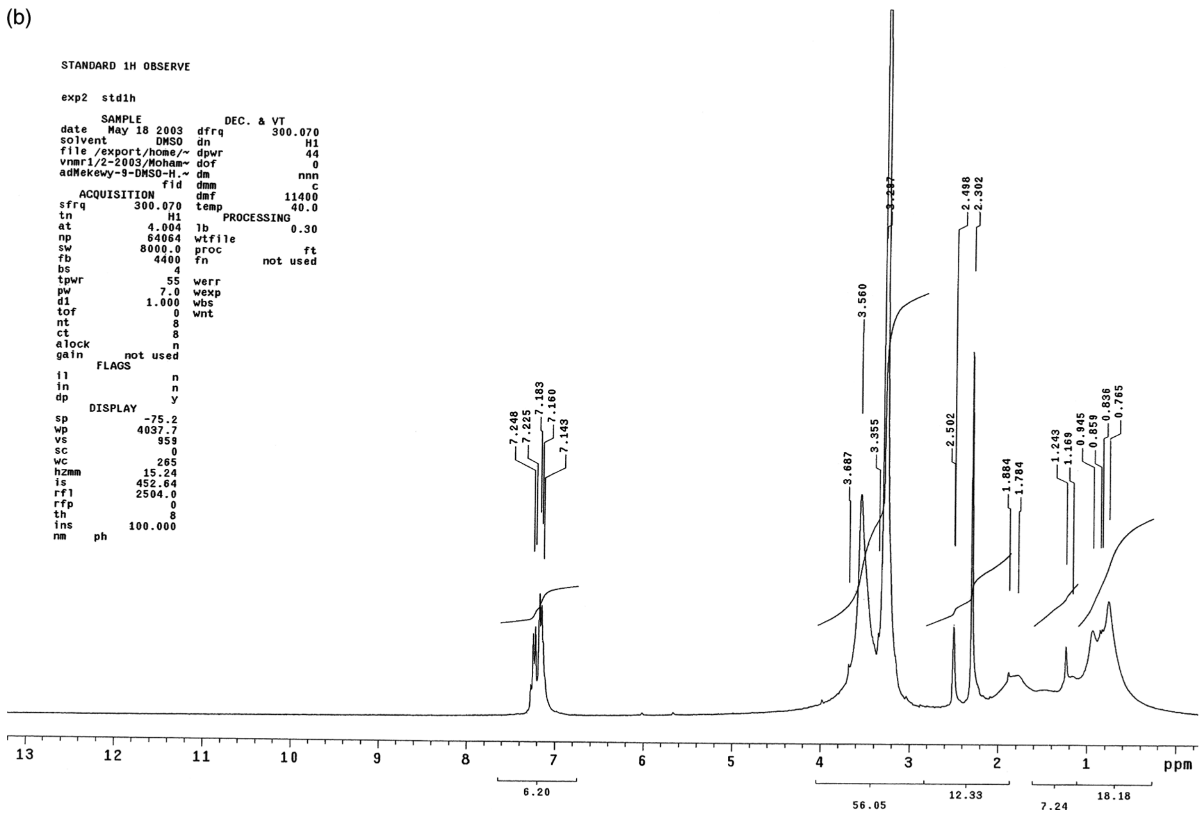

FIGURE 6 ^{1}HNMR of (a) Blank native PMMA; (b) PMMA prepared in presence of 400 ppm Ni (II) Salen complex compound; and (c) PMMA prepared in presence of 400 ppm Cr (III) Salen complex compound.



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STANDARD 1H OBSERVE

exp2  std1h

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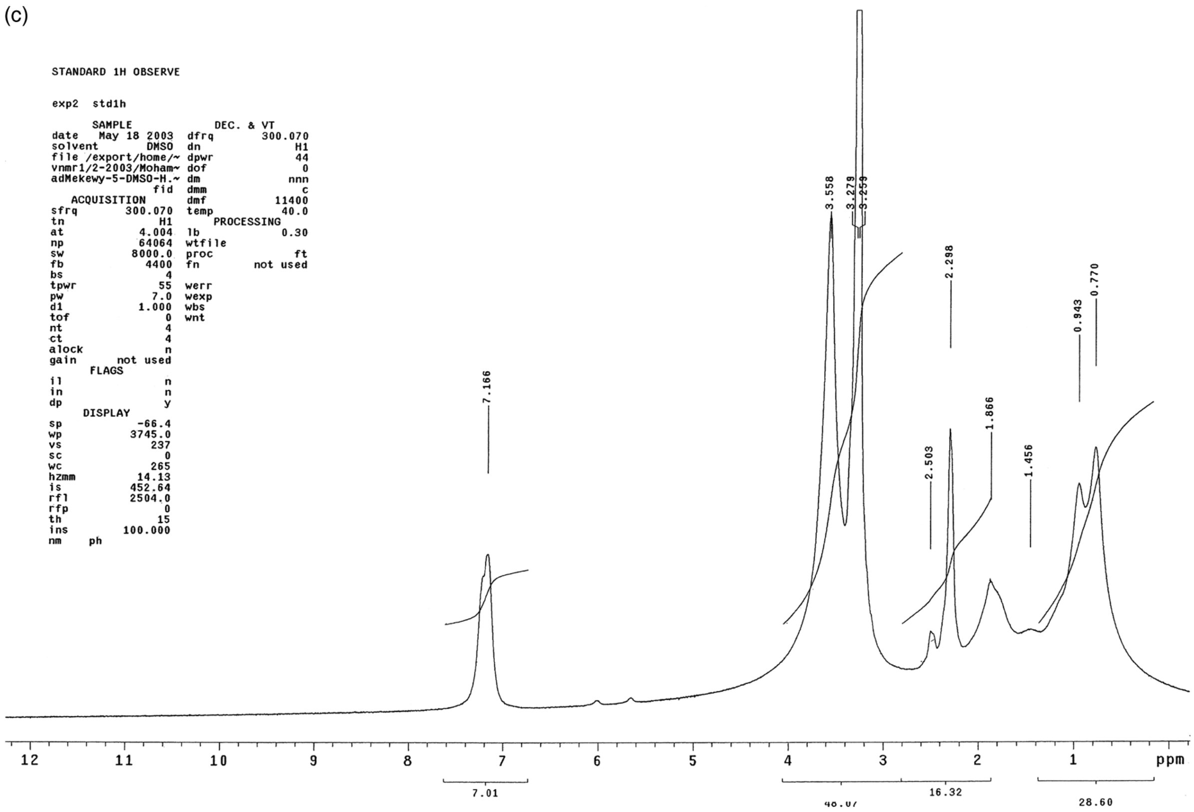
solvent       DMSO   dn              H1
file /export/home/~  dpwr            44
vnmr1/2-2003/Moham~  dof              0
adMekewy-9-DMSO-H.~  dm             nnn
               fid   dmm              c
   ACQUISITION       dmf          11400
sfrq       300.070   temp          40.0
tn              H1        PROCESSING
at           4.004   lb            0.30
np           64064   wtfile
sw          8000.0   proc            ft
fb            4400   fn        not used
bs               4
tpwr            55   werr
pw             7.0   wexp
d1           1.000   wbs
tof              0   wnt
nt               8
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp           -75.2
wp          4037.7
vs             959
sc               0
wc             265
hzmm         15.24
is          452.64
rfl         2504.0
rfp              0
th               8
ins        100.000
nm     ph
```

FIGURE 6 Continued.



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STANDARD 1H OBSERVE

exp2  std1h

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solvent        DMSO  dn             H1
file /export/home/~ dpwr            44
vnmr1/2-2003/Moham~ dof              0
adMekewy-5-DMSO-H.~ dm             nnn
                fid  dmm              c
   ACQUISITION      dmf          11400
sfrq        300.070  temp          40.0
tn               H1      PROCESSING
at            4.004  lb           0.30
np            64064  wtfile
sw           8000.0  proc           ft
fb             4400  fn       not used
bs                4
tpwr             55  werr
pw              7.0  wexp
d1            1.000  wbs
tof               0  wnt
nt                4
ct                4
alock             n
gain       not used
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in                n
dp                y
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sp            -66.4
wp           3745.0
vs              237
sc                0
wc              265
hzmm          14.13
is           452.64
rfl          2504.0
rfp               0
th               15
ins         100.000
nm    ph
```

FIGURE 6 Continued.

TABLE 2 Effect of UV Light Radiation on the Weight Average Molecular Weight of PMMA Prepared in Presence of Ni (II) and Cr (III) Salen Complex Compounds at Concentration Range of 200 to 400 ppm for 8 h at 80°C

	Exposure		M_w PMMA prepared using Ni (II) Salen		M_w PMMA prepared using Cr (III) Salen	
Catalyst concentration, ppm	Exposure time in minutes	Dose in Watt/cm^2	Before UV radiation	After UV radiation	Before UV radiation	After UV radiation
Zero catalyst	20	0.0166	433557	250060	—	—
Zero catalyst	30	0.025	—	—	—	—
200	60	0.05	985650	975650	880020	868670
300	180	0.15	1,552,469	1,535005	767550	750500
400	60	0.05	3,042,627	3,040062	1,021,988	1,019005
400	120	0.10	3,042,627	3,010520	1,021,988	1,019000
400	180	0.15	3,042,627	2,905478	1,021,988	1,018998

completely after less than 40 min whereas those prepared in presence of Ni (II) and Cr (III) Salen complex compounds proved to resist degradation due to a suppression of the UV radiation that may be due to an increased aromaticity [29]. The polydispersity had also increased after 3 h exposure to a maximum value of 1.712, which is still less than that, exhibited by native hompolymer. The PMMA preservation observed when prepared in presence of Ni (II) and Cr (III) Salen complex compounds indicates the suitability of such complex compounds as new catalysts that produce a polymer highly stable against UV light.

CONCLUSIONS

Poly(methyl methacrylate) prepared in the presence of Ni (II) and Cr (III) Salen complex compounds demonstrated unique molecular weight values. Cr (III) complex compounds exhibited better conversion yield level at different concentrations whereas Ni (II) complex compound exhibited a matching conversion yield only at 400 ppm. The activity of the Cr (III) Salen catalyst could be explained as due the presence of higher population of available active centers due to the different oxidation states characteristic for the Chromium. The Ni (II) Salen complex compound exhibited highest molecular weight value, which could be explained as due to the stability of the propagation step being higher than that for the Cr (III) Salen complex catalysts. PMMA samples prepared in the presence of 400 ppm of either Ni (II) or Cr (III) Salen complex compounds exhibited unique resistance toward UV irradiation up to 3 h, with only 2.4% loss in molecular weight value. Consequently, Ni (II) and Cr (III) Salen complexes are recommended as catalysts for the preparation of PMMA that is required to resist UV radiation, which allows applications as UV stable transparent polymer.

REFERENCES

[1] Takeuchi, D., Anada, K., and Oskada, K., *Macromolecules* **35**, 9628 (2002).
[2] Wang, J. S. and Matyjaszewski, K., *J. Am. Chem. Soc.* **117**, 5614 (1995).
[3] Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T., *Macromolecules* **28**, 1721 (1995).
[4] Kamigaito, M., Ando, T., and Sawamoto, M., *Chem. Rev.* **101**, 3689 (2001).
[5] Matyjaszewski, K., Ed. ACS Symposium series 768; *Am. Chem. Soc.* Washington, D.C. **101**, 3689 (2001).
[6] Matyjaszewski, K. and Xia, J., *Chem. Rev.* **101**, 2921 (2001).
[7] Sadek, E., Mekewi, M. A., Yehia, F. Z., Solyman, S. M., and Hassan, S. A., *Macromol. Chem. Phys.* **202**, 1505 (2001).
[8] Hanna, W. G., Mekewi, M. A., and El-Mosallamy, E. H., *J. Appl. Polym. Sci.* **82**, 562 (2001).
[9] El-Mosallamy, E. H., *J. Polym. Res.* **8**, 253 (2001).
[10] El-Mosallamy, E. H. and Mekewi, M. A., *Mat. Chem. and Phys.* **80**, 319 (2003).
[11] Mekewi, M. A., El-Mosallamy, E. H., and Hanna, W. G., *Cellulose Chem. and Tech.* **36**, 275 (2000).
[12] Neumann, A., Keul, H., and Hocker, H., *Macromol. Chem. Phys.* **201**, 980 (2000).
[13] Ueda, J., Kamigaito, M., and Sawamoto, M., *Polymer preprints* **37**, 272 (1996).
[14] Moineau, G., Minet, M., Dubois, P., Teyssie, P., Senninger, T., and Jerome, R., *Macromolecules* **32**, 27 (1999).
[15] Katsuki, T., *Coord. Chem. Rev.* **140**, 189 (1995).
[16] Srinivasan, K., Michaud, P., and Kochi, J. K., *J. Am. Chem. Soc.* **108**, 2309 (1986).
[17] Taqui Khan, M. M., Khan, N. M., and Boricha, A. B., *Inorg. Chim. Acta.* **174**, 175 (1990).
[18] Samsel, E. G., Srinivasan, K., and Kochi, J. K., *Am. Chem. Soc.* **108**, 7606 (1985).
[19] Blaawr, R., van der Baan, J. L., Balt, S., de Bloste, M. W. G., Klumpp, G. W., Koojiman, H., and Spek, A. L., *Inorganica. Chimica Acta* **336**, 28 (2000).
[20] Muller, J. G., Kayser, L., Paikoff, S. J., Durate, V., Tang, N., Perez, R. J., Rokita, S. E., and Burrows, C. J., *Coord. Chem. Reviews* **185–186**, 760 (1999).
[21] Maldanis, R., Wood, J. S., Chandosekaran, A., Rausch, M., and Chein, J. C., *J. Organometallic Chem.* **646**, 158 (2002).
[22] Shlyapintokh, V. Ya. and Gol'Denberg, V. I., *European Polymer Journal* **10**, 679 (1974).
[23] Achar, B. N., Fohlen, G. M., and Lokesh, K. S., *Polymer Degradation and Stability* **80**, 427 (2003).
[24] Calvin, C. and Bailes, D., *J. Am. Chem. Soc.* **68**, 953 (1946).
[25] Braun, D., Cherdron, H., and Kern, W. (1972). *Techniques of Polymerization Syntheses and Characterization*, (Wiley-Interscience, New York).
[26] Gipstein, E., Kiran, E., and Gilham, J. K., *ACS Polym. Prepr.* **13**, 121 (1972).

[27] Uegaki, H., Kotani, Y., Kamigaito, M., and Sawamoto, M., *Macromolecules* **30**, 2249 (1997).

[28] Sayyah, S. M., El-Shafiey, Z. A., El-Sockary, M. A., and Kandil, U. F., *Int. J. polym. Mater.* **51**, 225 (2002).

[29] Schauer, F., Kuritika, I., and Nespurck, N., *Polymer Degradation and Stability* **84**, 383 (2004).