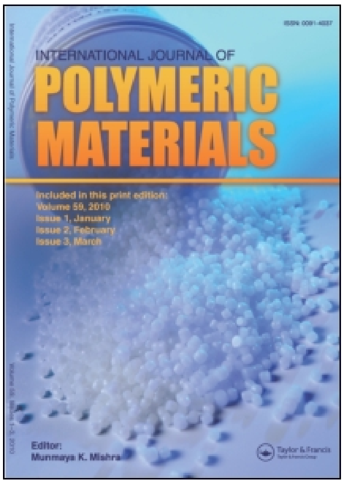

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Dithizone and carbazone complex compounds as initiators and γ -radiation anti-degradation agents for poly(methyl methacrylate)

Wageih G. Hanna[a]; Mohamed A. Mekewi[a]; El-Said H. El-Mosallamy[a]
[a] Department of Chemistry, Faculty of Science, Ain-Shams University, Cairo, Egypt

To cite this Article Hanna, Wageih G. , Mekewi, Mohamed A. and El-Mosallamy, El-Said H.(2003) 'Dithizone and carbazone complex compounds as initiators and γ -radiation anti-degradation agents for poly(methyl methacrylate)', International Journal of Polymeric Materials, 52: 6, 471 — 483

To link to this Article: DOI: 10.1080/00914030304911

URL: http://dx.doi.org/10.1080/00914030304911

International Journal of Polymeric Materials, 52: 471–483, 2003
Copyright © 2003 Taylor & Francis
0091-4037/03 $12.00 +.00
DOI: 10.1080/00914030390197734

DITHIZONE AND CARBAZONE COMPLEX COMPOUNDS AS INITIATORS AND γ-RADIATION ANTI-DEGRADATION AGENTS FOR POLY(METHYL METHACRYLATE)

Wageih G. Hanna
Mohamed A. Mekewi
El-Said H. El-Mosallamy
Department of Chemistry, Faculty of Science, Ain-Shams University,
Abbassia, Cairo, Egypt

It has been proved that lead dithizone and carbazone complex compounds act as adequate initiators and indicators for radical polymerization of methylmethacrylate. The color change observed during the polymerization process was attributed to the change in structure of the complex compounds according to tautomerization mechanism. Improvements to both polydispersity and relative crystallinity were observed in presence of lead dithizone and carbazone complex compounds. Better protection against gamma radiation was noticed ascertained through molecular mass measurements. A convincing reaction mechanism was also given.

Keywords: poly(methyl methacrylate); anti-degradation agents; lead dithizone; γ-radiation

INTRODUCTION

Dithizone [1] and carbazone are highlighted in the literature as specific reagents and indicators for the determination of many elements. The dithizone was reported as suitable reagent for determination of copper [2], mercury, lead and cadmium [3], iron and cobalt [4] palladium and platinum and their complexes [5, 6]. Identification of some transition metal complexes and mercury complex compound [6] and organo-tin compounds [7] were reported. A useful study was also made on the existence of a tautomeric equilibrium of dithizone [8] forms, which helps in emphasizing the proposed mechanism in the present

Received 21 February 2001; in final form 1 March 2001.

Address correspondence to Mohamed A. Mekewi, Department of Chemistry, Faculty of Science, Ain-Shams University, Abbassia, Cairo, Egypt.

work. Metal dithizonates when used as dopants for poly(methylmethacrylate) were proved highly resistant to UV accompanied with color changes as reaction proceeds [9]. Carbazone also were reported as reagent for the determination of trace amounts of tin, molybdenum, mercury [10–12], cobalt [13] and nickel [14] metals and ions. In a recent publication aryl and alkyl derivatives of Bi, Sb and As, were proved as adequate for the radical polymerization of vinyl monomers [15].

Accordingly, it was desired to study the role of lead dithizone and carbazone complexes as initiators for methylmethacrylate polymerization and also their function as indicators for free radicals occurring during the process. The pattern changes of molecular mass, polydispersity, tacticity and crystallinity were carefully followed with attention given to significant protection against gamma radiation degradation.

MATERIALS AND EXPERIMENTAL

Lead Dithizone and Carbazone Complexes Structure and Stability

The lead complex compounds were prepared as reported by Oelschager *et al.* [16] with affirmed structures as shown in Figure 1. Thermal gravimetric analyses (TGA) for the two complexes were carried out using TGA-50 derivatograph of Shimadzu Corp. (Japan) performed in nitrogen atmosphere at a heating rate of 10°C/min. TGA measurements were pre-determined to ensure complexes stability during the polymerization process temperature used.

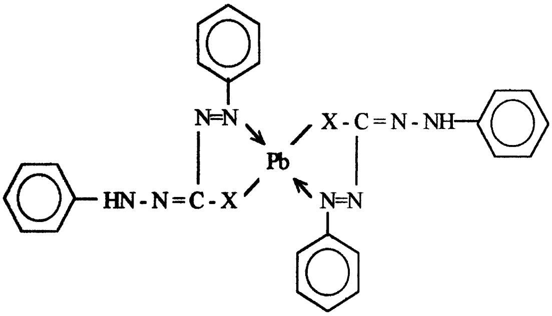

FIGURE 1 Lead complex structure (whereas X = S for dithizone and X = O for carbazone).

Polymer Synthesis and Film Formation

Polymer samples were prepared at 80°C in bulk by mixing purified and dried methyl methacrylate monomer with lead dithizone or carbazone complexes at different concentrations. The mixture was mixed in a glass ampoule under vacuum and sealed prior to subjecting to polymerization temperature for periods of time ranging from 1 hour to 8 hours. The polymer samples were dissolved in toluene and then the polymer solution was collected and cast onto glass dishes to form transparent films with a thickness of $\sim$1 mm. The cast films were dried under ambient conditions for 24 h and then placed in a vacuum oven at 70°C to remove residual solvent. The conversion yield % was calculated as the ratio of polymer weight compared to monomer weight used. The cast films were subjected to the various studies proposed.

Polymers Molecular Weight and Structure Studies

Polymer molecular weight values (M_w and M_n) and polydispersity were determined by Gel Permeation Chromatography (GPC) using high pressure GPC (Waters) with differential refractometer type M 2410 as the detector. Polydispersity of polymer products were calculated using Millennium 23 chromatography manager with Gel permeation application software. The polymer structure was routinely confirmed using FT-IR 1650 Perkin Elmer Fourier Transform Infrared spectrophotometer in KBr disc. Tacticity of the polymer product was also examined using H^1-NMR using Spectrospin-Brucker AC 200 MHz NMR spectrometer. Variations of the amorphous and crystalline patterns of the polymer product were pursued utilizing Philips X-ray diffractometer model PW 1140/90 (Fe-filter and CoKα radiation). The X-ray patterns were recorded automatically with a scanning speed of 2°/min and a scanning angular range (2θ) from 5 to 45°.

Color Change Follow-Up

Color detection and changes of all samples were followed-up using UV-visible spectrophotometer Unciam (-Helios in the range of 200–700 nm with CCl_4 as solvent.

Gamma Irradiation Source and Doses

Irradiation of film specimens was carried out at various doses of γ-rays. Access to the source of Co 60-gamma, at a dose rate of 0.45 Mrad/hour was allowed by the National Center for Radiation Research and Technology, Nasr City, Cairo.

RESULTS AND DISCUSSION

Thermal Stability Studies of Lead Dithizone and Carbazone

The thermal gravimetric analysis (TGA) of lead dithizone complex compound [$Pb(C_{13}H_{11}N_4S)_2$] proved its dissociation in three major steps in the temperature range 120– 687°C followed by a plateau from 687–1000°C. The weight loss values during thermal degradation are summarized in Table 1. Stoichiometric calculations according to these values lead to the proposed fragmentation scheme, Figure 2. Lead carbazone [$Pb(C_{13}H_{11}N_4O)_2$] dissociated in 4 major steps in the temperature range 100–700°C with a final plateau at 700–1000°C. From the TGA results it is evident that both complexes start to dissociate thermally well above the temperature necessary for the polymerization process (*i.e.*, 80°C). In this respect dithizone starts to dissociate at a temperature of 120°C while that of carbazone starts to dissociate at about 100°C indicating high stability of the lead-sulfur bond compared to lead-oxygen bond in the carbazone. Both lead complexes were found to dissociate completely at about 700°C. The TGA results encouraged the use of such lead complexes for the present work insuring their fragmentation to lead oxide and further to pure lead metal at the elevated temperature of 700°C.

Polymer Yield %, Molecular Weight, and Polydispersity

The percentage of conversion of monomer to polymer in presence of lead complex compounds were found to vary from 80 to 95% compared to that prepared by pure thermal polymerization which was only 85%.

TABLE 1 Thermal Fragmentation of Lead Complex Compounds from Thermal Gravimetric Results

Molecular formula	Molecular weight	Fragment step	Temperature range (°C)	Loss % calcd.: found	Significance of loss
[$Pb(C_{13}H_{11}N_4S)_2$]	717.5	I	120:228	23.9:23.7	$(SCN_3)_2$
		II	228:329	21.5:20.7	$(C_6H_5)_2$
		III	329:687	25.7:25.9	$(C_6H_6N)_2$
		*	687:1000	28.9:29.4	Pb
[$Pb(C_{13}H_{11}N_4O)_2$]	685.5	I	100:188	12.8:12.2	$(N_2O)_2$
		II	188:218	22.5:22.7	$(C_6H_5)_2$
		III	218:290	12.0:12.8	$(CHN_2)_2$
		IV	290:700	22.5:22.0	$(C_6H_5)_2$
		*	700:1000	30.2:30.0	Pb

* Plateau for the formation of the metal from the complex.

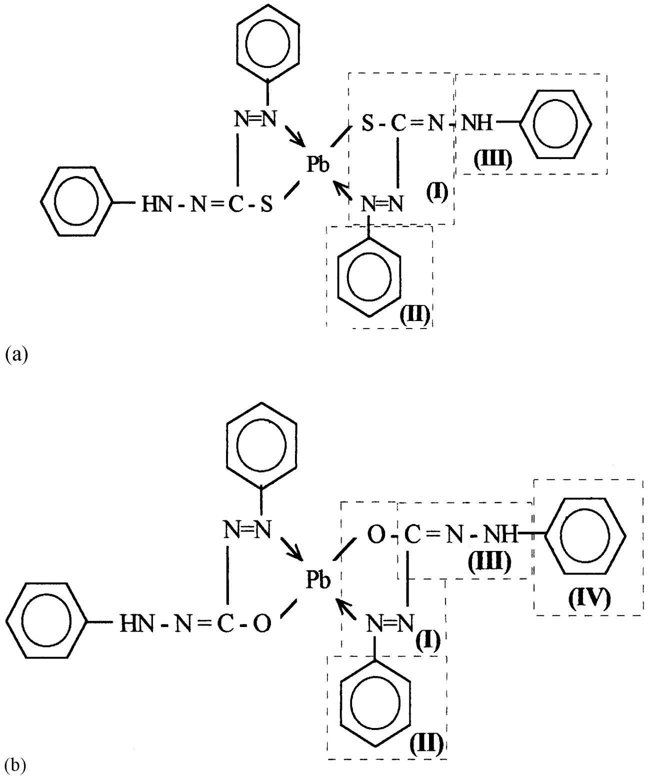

FIGURE 2 Schematic fragmentation of: (a) Lead dithizone complex compound; (b) Lead carbazone complex compound.

From Table 2, it is obvious that the polymerization process is delayed by an induction period as the complex compound concentration is increased. While the lead complex compounds exhibited decrease for the polymerization rate process, improved polydispersity was observed, Table 3. Those findings indicate the function of the complex compounds as chain transfer agents regulating the chain growth pattern better than that at zero concentration.

Polymer Structure and Crystallinity

The polymer structure was confirmed using FT-IR, Figure 3. No apparent change in the balance of either form of tacticity, *i.e.*, isotactic, heterotactic and syndiotactic; seems to prevail as illustrated from the IR spectrum of all samples in presence and absence of the complex compounds compared to IR identification reported by

TABLE 2 Effect of Lead Complex Concentrations on Molecular Weight Values of MMA Polymerization

	Polymerization time (hours)						
Complex Conc. (μM)	2	3	4	5	6	7	8
Pb dithizone							
Zero	342,180	544,970	606,640	710,150	–	–	840,330
200	78,180	128,430	204,180	288,600	323,130	365,1120	560,900
700	–	109,950	171,840	212,850	286,220	369,840	485,350
1400	–	94,500	134,230	206,980	258,190	312,880	430,130
2000	–	–	100,740	150,130	205,340	290,710	400,150
Pb carbazone							
Zero	342,180	544,970	606,640	710,150	–	–	840,330
200	–	91,470	171,880	252,470	294,200	314,620	395,600
700	–	63,490	142,000	202,070	216,150	259,440	328,720
1400	–	–	115,360	149,240	178,570	233,260	268,260
2000	–	–	95,400	110,510	155,280	210,420	235,480

O'Reilly [17]. The syndiotactic structure is recognized at the absorption bands of 1485, 1450, 1438, 1388, 1270, 1240 cm^{-1} while that of the isotactic structure is distinguished at 1465, 1260, and 1252 cm^{-1}. The other bands shown are considered as common between the two tactic structures as indicative for the (C–H), (C=O), skeletal, (CH_3–O) and the (a–CH_3) groupings. To gain further

TABLE 3 Variation of Polydispersity, Tacticity, and Relative Degree of Crystallinity for PMMA with Lead Complex Concentrations

		Tacticity (%)			
Complex Conc. (μM)	Degree of Dispersity	Isotactic	Heterotactic	Syndiotactic	Relative degree of Crystallinity (%)
Zero	1.76	6.0	41.8	52.2	amorphous
Pb dithizone					
200	1.60	7.1	37.2	55.7	70
700	1.52	6.7	38.1	55.2	75
1400	1.41	6.1	41.8	53.1	78
2000	1.30	5.7	41.0	53.3	79
Pb carbazone					
200	1.69	6.9	39.7	53.4	62
700	1.65	6.5	40.4	53.1	68
1400	1.60	6.0	42.0	52.0	70
2000	1.54	5.9	41.4	52.7	72

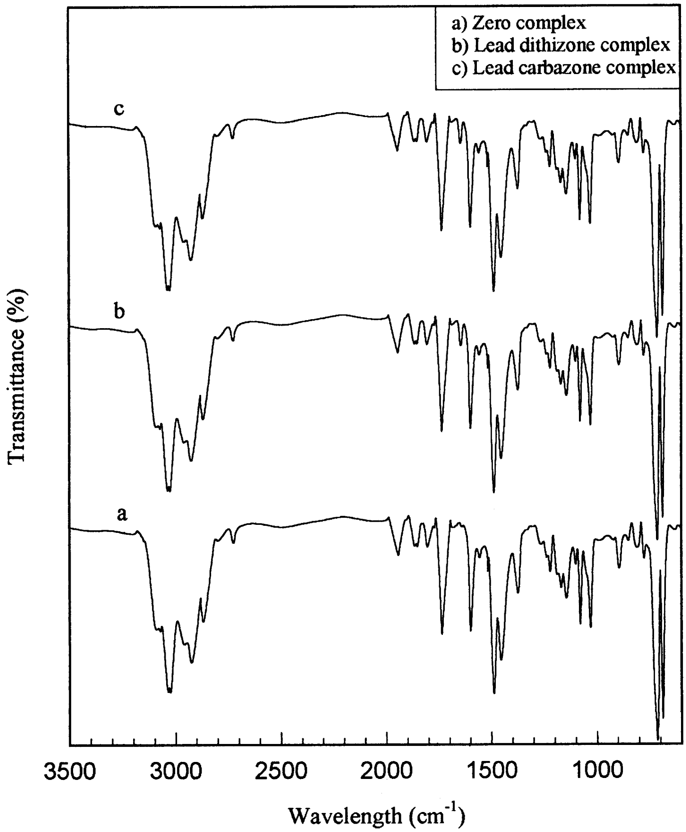

FIGURE 3 FT-IR spectral analysis of PMMA in presence and absence of lead complex compounds.

information about the polymer products tacticity, HI-NMR analysis was carried out the results of which are shown in Table 3. It is confirmed once more that the tacticity ratio of either tactic structure in presence and absence of lead complex compounds employed as initiators, did not dramatically change. Surprisingly, however, X-ray studies revealed an improved order of polymer chains prepared in presence of the lead complexes. This is confirmed by the appearance of three reflexes at $2\theta = 15$, 30 and 42° for the lead dithizone and 16, 30 and 41° for the lead carbazone, while pure polymer are nearly amorphous, Figure 4. The amorphous conduct during chain growth may be due to the fast precipitation of the growing chains due to ionic crosslinking leaving the system no time to give a crystalline

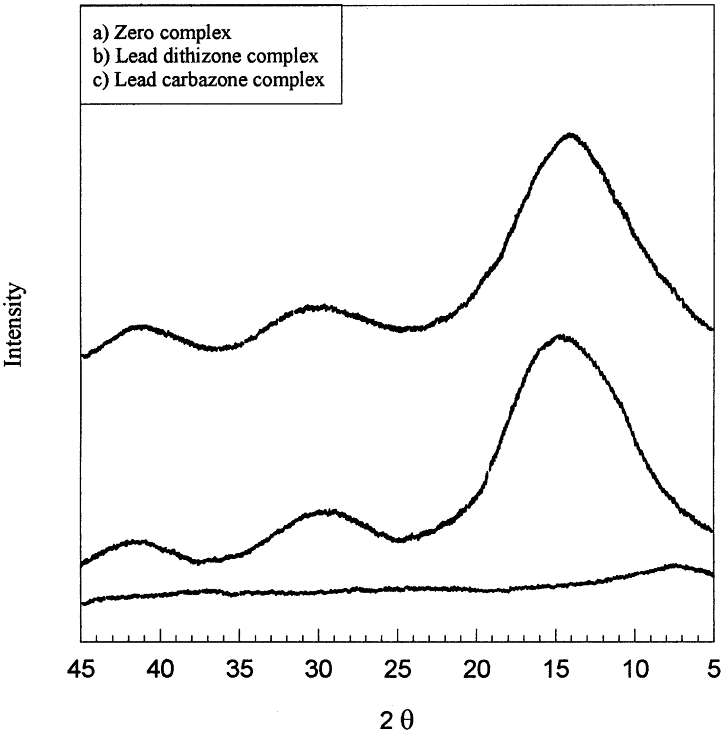

FIGURE 4 X-ray diffraction patterns for PMMA in presence and absence of lead complex compounds.

phase [18]. The presence of either lead complex seem to impart a regulating effect to the growing polymeric chains due to their ability of capturing free radicals produced during the reaction. The free radicals capturing involvement is accompanied by a color change from red to yellow, which is mainly due to the tautomeric change of the azo to a hydrazo form. This proposed conduct allows the growing polymer chains more time to crystallize in the presence of the lead complex compounds than in their absence. The relative degree of crystallinity (or order!) was also calculated [19] for all samples and are given in Table 3. As shown, as lead complex concentration increase an improvement in the relative degree of order are noticed. Lead dithizone exhibited, in general, highest relative degree of crystallinity compared to lead carbazone. This behavior may be explained by the lead dithizone complex higher stability compared to the carbazone structure [20].

Color Change and Reaction Mechanism

The molar absorbtivity of lead dithizone in CCl_4 equals 6.88×10^4 at $\lambda_{max} = 520$ nm while for lead carbazone it equals 7.20×10^4 ($a = 0.35$) at $\lambda_{max} = 508$ nm, (CT band). Lead dithizone in CCl_4, however, exhibits distinctive absorption bands at 500 nm and 300 nm, Figure 5a, mainly due to the Azo- structure, Figure 1. On the other hand, polymer samples prepared in the absence of any initiators showed no specific features of absorption due to the absence of any foreign or coloring materials, Figure 5d. However, in presence of lead dithizone complex compound; as initiator; a color change was observed with absorption bands at 300 nm, Figure 5c, accompanied by a new shoulder at

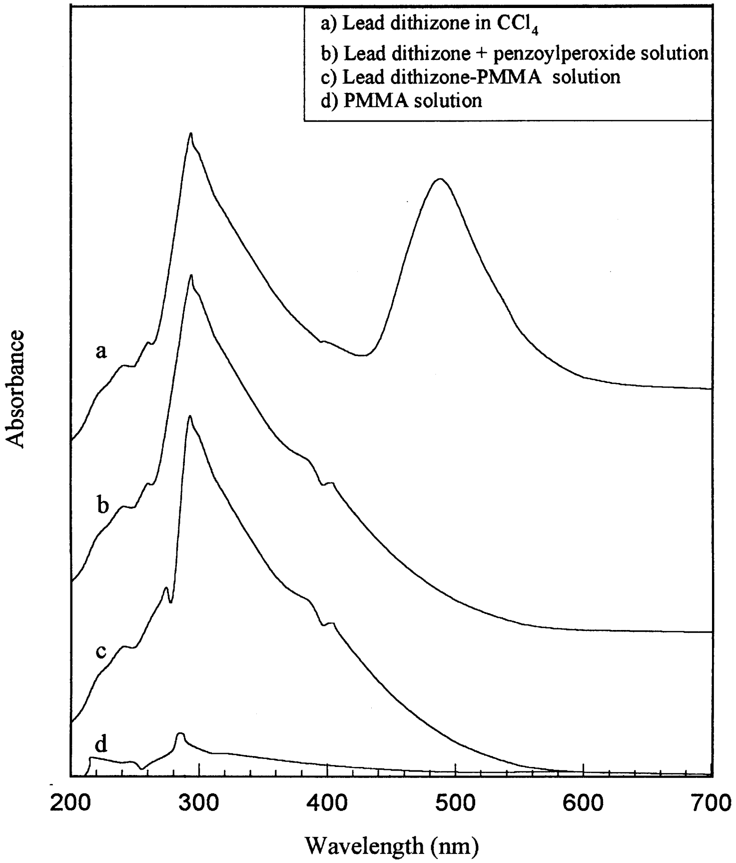

FIGURE 5 UV visible spectral analysis for lead dithizone in absence and presence of MMA using different radical sources.

405 nm. Such color change is believed to be attributed to the formation of an Azo-free radical structure. The disappearance of the absorption band at 500 nm (CT band) accompanied by the developing of yellow color is believed to be due to the decrease of the original Azostructure and the formation of a stable structure of the benzenoid ring at 300 nm [21, 22]. This phenomena of color change due to structure variation of lead dithizone and carbazone complexes was confirmed experimentally by using a free radical source in medium such as benzoyl peroxide. When benzoyl peroxide was added to lead complex the color changed from red to yellow with the disappearance of that band at 500 nm and the production of a new shoulder at 405 nm, Figure 5b. Such color change is mainly attributed to the formation of peroxo-complex *via* azo group, which helps to suggest the following:

Lead dithizone is present in two tautomeric forms only when free radicals are present in the medium as evidenced elsewhere [21,22]. In conclusion, the polymerization process of methyl methacrylate if made in presence of lead dithizone complex compound proceeds *via* free radical mechanism, which is evidenced by an associated color change. Color changes observed as the polymerization process is completed are explained as due to the transformation of the Azo- group of the lead dithizone complex to a stable bidentate chelated polymer complex compound. Such experimental findings helped constructing an overall free radical polymerization mechanism convincingly presented in Figure 6.

Gamma Irradiation and Protection Optimization

The degradation of different poly(methyl methacrylate) samples prepared in absence and presence of lead complexes was investigated using gamma irradiation at doses from 0.5 to 3 Mrads. The degradation scheme was followed-up as a function of the molecular weights reduction Table 4. As illustrated from the results, increase of radiation dose leads to increase percentage loss of the molecular weights for the PMMA prepared in absence of lead complexes up to 85% at 3 Mrads. In presence of either lead complex, protection against damage and degradation by gamma was clearly observed as the percent of chain damage has decreased to 53% instead. This is explained as due to the increased degree of the polymer order at the expense of the amorphous regions which are the most susceptible regions for degradation by gamma radiation [23]. Lead dithizone, as initiator, exhibited preferential protection against gamma radiation compared to the lead carbazone complex due to dithizone higher stability [19].

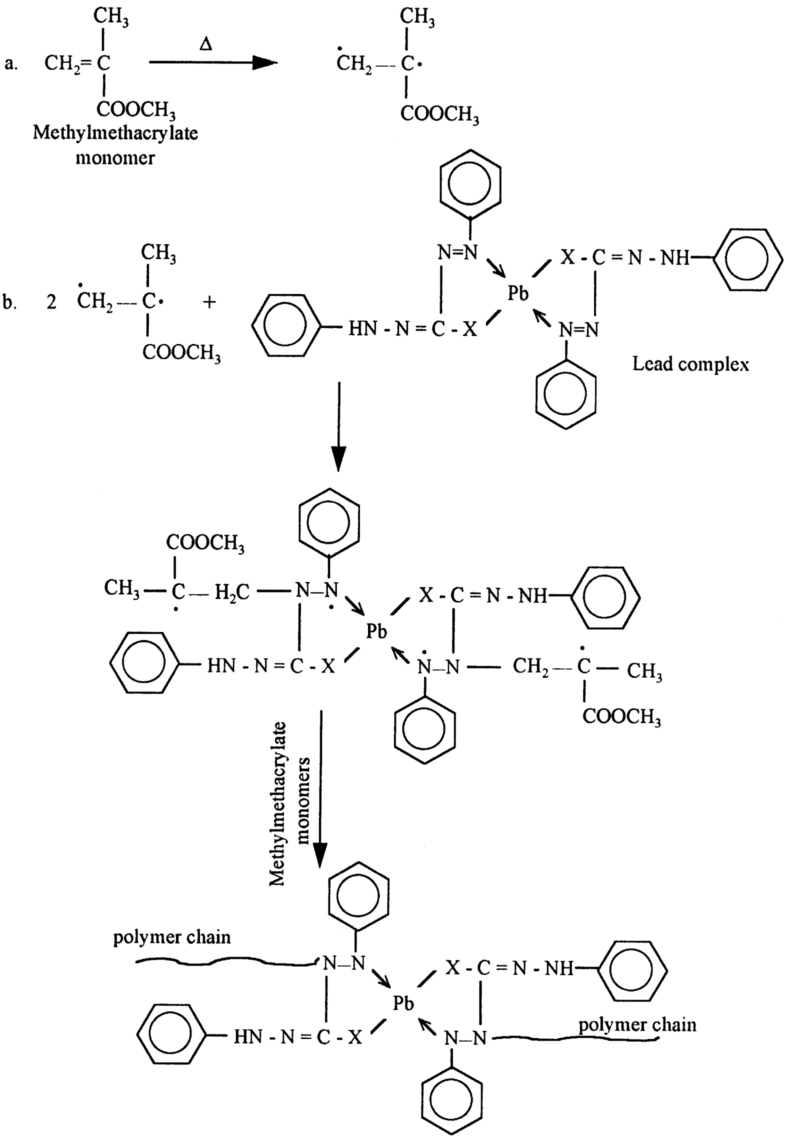

FIGURE 6 Schematic reaction mechanism of MMA polymerization in presence of lead complex compound as initiators.

TABLE 4 Effect of Lead Complex Concentrations on the Molecular Weight Loss for PMMA at Different γ-Radiation Doses

Complex conc. (μM)	Molecular weight loss %/irradiation dose(Mrad)			
	0.5	1.0	2.0	3.0
Zero	40	53	71	85
Pb dithizone				
200	38	49	66	75
700	35	45	60	69
1400	30	41	52	61
2000	27	33	45	53
Pb carbazone				
200	38	50	66	77
700	36	47	62	72
1400	32	42	55	65
2000	28	37	49	58

CONCLUSION

Lead dithizone and carbazone complex compounds when present during the bulk polymerization of methyl methacrylate proved adequate as initiators exhibiting a conversion yield of 80–95%. The lead complex compounds have proved suitable as indicators for the free radical mechanism for the polymerization reaction. The dithizone and carbazone complexes have proved to regulate polymer chain lengths through chain transfer mechanism and also as protecting agents and colorants for the end polymer product. The color change/structure relation through tautomerization free radical polymerization was also proposed. Increased order and orientation of the formed chains would resist UV irradiation as reported earlier [9]. A suggested two-arm metalo poly(methyl methacrylate) formation should function more selectively in increasing the polymer anti-degradation properties, a matter that deserves to be looked at more closely in future works.

REFERENCES

[1] Federov, L. A. and Rebrov, A. I. (1992). *Izv. Akad. Nauk SSSR. Ser. Khim*, (1), pp. 113–17.

[2] Kumar, B., Singh, H. B., Katyal, M. and Sharma, R. L. (1991). *Mikrochem. Acta*, **3**(103), 79087.

[3] Kardivarenko, L. M., Shkinev, V. M., Spikvakov, B. Ya., Bagreev, V. V., Yurtov, E. V. and Koroleva, M. Yu. Zh. (1991). *Zh. Neorg. Khim.*, **36**(7), 1887–90.

[4] Dawson, M. V. and Lyle, S. J. (1990). *Talanta*, **37**(12), 1189–1.

[5] Stanislaw, K. and Zygmunt, M. (1987). *Analyst*, **112**(11), 1503–1506.

[6] Michalska, D. and Kowal, A. T. (1985). *Spectrochim. Acta Part A*, **41A**(10), 1119–25.

[7] Mitsubishi Heavy Industries, Ltd. Japan Kokai Tokyo Koho JP 58,171,667 [83,171,667] (1983).

[8] Hutton, A. L. (1987). *Polyhydron*, **6**(1), 13–23.

[9] Moharram, M. A., Shabaka, A. and Khafagi, M. G. (1991). *J. Appl. Polym. Sci.*, **42**(8), 2121–8.

[10] Das, H. K. and Kaimal, K. G. (1983). *J. Indian Chem. Soc.*, **60**(10), 1004–6.

[11] Ohashi, K. and Yamamoto, K. (1984). *Bunseki Kagaku*, **33**(2), E77–E80.

[12] Labuda, J. and Plaskon, V. (1990). *Anal. Chim. Acta*, **228**(2), 259–63.

[13] Chen, G., Yan, X. and Nie, X. (1989). *Gaodeng Xuexiao Huaxue Xuebao*, **10**(2), 200–2.

[14] Sarmah, K. and Das, H. K. (1987). *J. Indian Chem. Soc.*, **64**(7), 449–51.

[15] Grishen, D. F. and Moikin, A. A. (1998). *Vyskomol. Soedin*, *Ser. A Ser. B*, **40**(8), 1266–1270.

[16] Oelschager, W. and Schwarz, E. (1972). *Z. Anal. Chem.*, **258**, 203.

[17] O'Reilly, J. M. and Mosher, R. A. (1981). *Macromolecules*, **14**, 602.

[18] Scwarzenbacher, G., Saf, R., Schitter, R. and Hummel, K. (1999). *Synthetic Metals*, **101**, 143–144.

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

[20] Smith, R. M. and Martell, A. E., *Critical Stability Constants*, Vol. 1–6, Pelsun, New York, 1989.

[21] Diaz, F. R., Sanchez, C. O., del Valle, M. A., Uglade, L. and Gargallo, L. (1999). *Synthetic Metals*, **105**, 161–169.

[22] Hirao, T., Yamagushi, S. and Fukuhara, S. (1999). *Synthetic Metals*, **106**, 67–70.

[23] Morton, M. and Fettes, L. (1964). *J. Polym. Sci.*, **A2**, 3311.