# Polymerization of Methylmethacrylate Monomer in the Presence of Dithizone and Carbazone Complexes

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**ABSTRACT:** It has been proved that lead dithizone and carbazone complexes act as adequate initiators for radical polymerization of methylmethacrylate and also as reliable indicators for the free-radical mechanism. Lead dithizone complex, in particular, exhibited the phenomenon of color change during the polymerization process, suggesting the use of this complex as a free-radical indicator and also as a coloring material for acrylic polymers *in situ*. The color change observed during the polymerization process was attributed to the change in the structure of complex compounds according to a tautomerization mechanism. The presence of lead dithizone and carbazone complexes as initiators exhibited reduced molecular mass compared to those prepared in their absence, indicating their role as regulating agents during the polymerization process. The polydispersity and tacticity parameters were measured through the present work using GPC and $^1$H–NMR techniques, respectively. The amorphous nature of polymer chains in both the absence and the presence of the lead dithizone and carbazone was studied using X-ray diffraction, where an increased crystallinity was observed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 562–568, 2001

**Key words:** methylmethacrylate; dithizone; carbazone; polymerization; polydispersity; tacticity

## 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 a suitable reagent for the determination of copper[2]; mercury, lead, and cadmium[3]; iron and cobalt[4]; and palladium and platinum and their complexes.[5,6] Identification of some transition metal complexes and mercury complex compound[6] and organotin compounds[7] was reported. A useful study was also made on the existence of a tautomeric equilibrium of dithizone[8] forms, which helps in emphasizing the pro-

posed mechanism in the present work. When used as dopants for polymethylmethacrylate, metal dithizone complexes proved to be highly resistant to UV, accompanied by color changes as the reaction proceeds.[9] Carbazone was also reported as a 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] The attention focused on this class of materials, however, indicates that there is still a need to uncover even more information about their role during polymerization and their effect on polymer product characterization.

Accordingly, we set out to study the role of these complexes as initiators during polymerization reactions and also their function as indica-
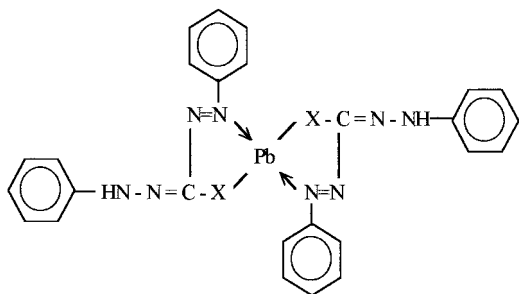
**Figure 1**   Lead complex structure (X = S for dithizone and X = O for carbazone).

tors for free radicals. Their functions as colorants for produced polymers and aftereffects on crystallinity were studied with particular attention paid to variations in molecular mass, polydispersity, and tacticity.

## EXPERIMENTAL

### Structure and Stability of Lead Dithizone and Carbazone Complexes

The lead complex compounds were prepared as reported by Oelschager and Schwarz[16] with an affirmed structure as shown in Figure 1.

Thermal gravimetric analyses (TGA) for the two complexes were carried out using TGA-50 derivatograph of Shimadzu Corp. (Japan). Measurements were performed in nitrogen atmosphere at a heating rate of 10°C/min. TGA measurements were employed to ensure stability of the complexes at temperatures used during the polymerization process.

### Synthesis of Polymers

Polymethylmethacrylate (PMMA) samples were prepared at 80°C in bulk by mixing purified and dried methylmethacrylate with lead dithizone or carbazone complexes as initiators at a concentration range of 0.05 to 0.15% (w/w). The mixture was prepared in a glass ampoule under vacuum and sealed prior subjecting to polymerization temperature, for periods of time ranging from 1 to 24 h. The polymer samples were dissolved in toluene and the polymer was recovered using methyl alcohol. The precipitated polymers were filtered and dried under vacuum at 70°C for 24 h; the yield percentage was finally weighted and calculated with respect to the polymerization yield.

### Molecular Weight and Structure Studies of Polymers

The PMMA molecular weight values ($M_w$ and $M_n$) and their polydispersity were determined by gel-permeation chromatography (GPC) using high-pressure GPC (Waters Instruments, Rochester, MN) with a differential refractometer type M 2410 as the detector. Polydispersity values of polymer products were accordingly calculated using Millennium 23 chromatography manager with gel-permeation application software. The polymethylmethacrylate structure was routinely confirmed using FTIR 1650 Perkin–Elmer Fourier transform infrared spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT) in KBr disc. In this respect, the polymer solution was affixed dropwise on the KBr disc, after which the solvent was evaporated under vacuum to complete dryness of the disc prior to investigation.

**Table I   Thermal Fragmentation of Lead Complexes from Results of Thermal Gravimetric Analysis**

| 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) | $(C_6H_6N)_2$ |
| | | a | 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) | $(C_6H_5)_2$ |
| | | a | 700–1000 | 30.2 : (30.0) | Pb |

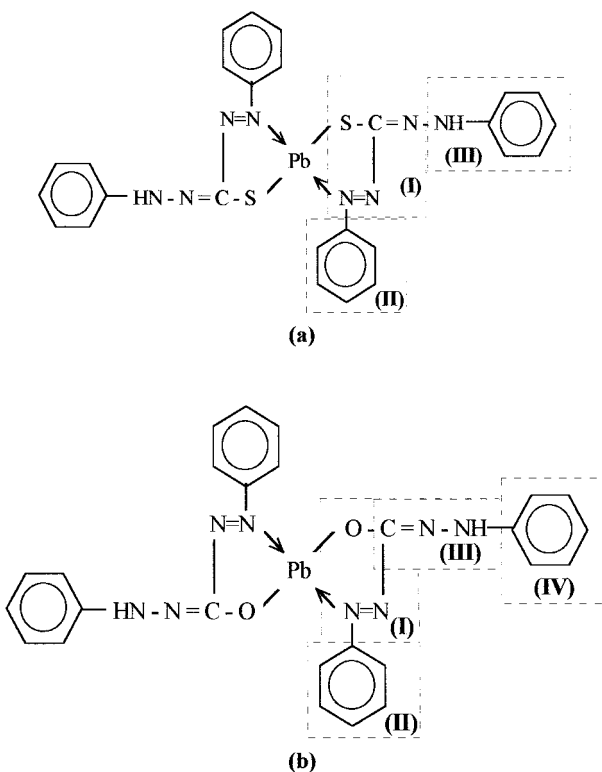a Formation of the metal from the complex.

**Figure 2** Schematic fragmentation of: (a) lead dithizone complex; (b) lead carbazone complex.

Tacticity of the polymethylmethacrylate was investigated using ^{1}H–NMR using Spectrospin-Bruker AC 200-MHz NMR spectrometer (Bruker Instruments, Billerica, MA).

Variations of the amorphous pattern of the polymer product were pursued utilizing Philips X-ray diffractometer model PW 1140/90 (Philips, The Netherlands) using Fe-filter and $CoK_\alpha$ radiation. The X-ray patterns were recorded automatically with a scanning speed of 2°/min and a scanning angular range ($2\theta$) from 5 to 60°. Transparent polymer films with a thickness of about 1 mm were prepared and used for the X-ray studies. The polymer solution of different samples in toluene was cast onto glass dishes. 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 to constant weight before being investigated.

## Color Change Follow-up

As the polymerization process proceeded color changes were followed up by a UV-visible spectrophotometer Unciam $\alpha$-Helios in the range of 200–700 nm using $CCl_4$ as solvent.

## RESULTS AND DISCUSSION

### Thermal Stability Studies of Lead Dithizone and Carbazone Complexes

The thermal gravimetric analysis (TGA) of lead dithizone complex $[Pb(C_{13}H_{11}N_4S)_2]$ proved its dissociation at three major steps in the temperature

**Table II   Effect of Lead Complex Concentrations on Molecular Weight Values of MMA Polymerization**

| Time (h) | Blank Sample (Zero Complex) $M_w$[c] | $M_n$[c] | 0.05% Pb(HDz)$_2$[a] $M_w$ | $M_n$ | 0.10% Pb(HDz)$_2$ $M_w$ | $M_n$ | 0.15% Pb(HDz)$_2$ $M_w$ | $M_n$ | 0.05% Pb(HCz)$_2$[b] $M_w$ | $M_n$ | 0.10% Pb(HCz)$_2$ $M_w$ | $M_n$ | 0.15% Pb(HCz)$_2$ $M_w$ | $M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 177.30 | 100.70 | 58.80 | 36.70 | — | — | — | — | — | — | — | — | — | — |
| 5 | 342.20 | 194.50 | 78.20 | 49.50 | 57.40 | 36.20 | 52.00 | 33.10 | 41.50 | 23.80 | 31.50 | 18.30 | — | — |
| 6 | 545.00 | 310.00 | 128.40 | 81.80 | 110.00 | 70.40 | 94.50 | 61.60 | 71.90 | 42.00 | 52.10 | 30.60 | 25.80 | 15.00 |
| 7 | 606.60 | 345.00 | 204.20 | 131.30 | 171.80 | 112.90 | 107.60 | 72.10 | 119.30 | 70.40 | 75.50 | 44.80 | 31.40 | 18.50 |
| 8 | — | — | 288.60 | 186.10 | 212.90 | 143.00 | 134.20 | 91.70 | 152.50 | 90.50 | 99.40 | 59.50 | 49.20 | 29.40 |
| 9 | — | — | 323.10 | 210.90 | 227.70 | 155.60 | 165.60 | 116.50 | 171.40 | 102.10 | 142.50 | 86.00 | 53.60 | 32.30 |
| 10 | — | — | 408.30 | 267.50 | 286.20 | 199.70 | 207.00 | 150.50 | 194.20 | 116.20 | 162.20 | 99.00 | 78.60 | 47.80 |
| 12 | — | — | — | — | 369.80 | 262.30 | 258.20 | 194.30 | 214.60 | 129.40 | 197.40 | 122.20 | 133.30 | 83.70 |
| 14 | — | — | — | — | — | — | 312.90 | 240.50 | — | — | — | — | 156.90 | 100.10 |
| 16 | — | — | — | — | — | — | — | — | — | — | — | — | 184.70 | 119.20 |
| 24 | 840.30 | 478.00 | 570.00 | 374.00 | 485.40 | 345.40 | 430.10 | 331.60 | 295.60 | 178.70 | 283.00 | 177.50 | 268.30 | 174.40 |

[a] Pb(HDz)$_2$ = Lead dithizone complex.
[b] Pb(HCz)$_2$ = Lead carbazone complex.
[c] $M_n$ and $M_w$ = value $\times 10^3$.

**Table III   Variation of Polydispersity of PMMA with Lead Complex Concentrations**

| Time (h) | Blank Sample | Lead Dithizone Complex Concentrations | | | Lead Carbazone Complex Concentrations | | |
|---|---|---|---|---|---|---|---|
| | | 0.05% | 0.10% | 0.15% | 0.05% | 0.10% | 0.15% |
| 4 | 1.77 | 1.60 | — | — | — | — | — |
| 5 | 1.76 | 1.58 | 1.59 | 1.57 | 1.74 | 1.72 | — |
| 6 | 1.76 | 1.57 | 1.56 | 1.53 | 1.71 | 1.70 | 1.72 |
| 7 | 1.76 | 1.55 | 1.52 | 1.49 | 1.69 | 1.69 | 1.70 |
| 8 | — | 1.53 | 1.49 | 1.46 | 1.68 | 1.67 | 1.67 |
| 9 | — | 1.52 | 1.46 | 1.42 | 1.68 | 1.66 | 1.66 |
| 10 | — | — | 1.43 | 1.38 | 1.67 | 1.64 | 1.64 |
| 12 | — | — | 1.41 | 1.33 | 1.66 | 1.62 | 1.59 |
| 14 | — | — | — | 1.30 | — | — | 1.57 |
| 16 | — | — | — | — | — | — | 1.55 |
| 24 | 1.76 | 1.52 | 1.41 | 1.30 | 1.65 | 1.60 | 1.54 |

range 120–687°C, followed by a plateau from 687 to 1000°C. The weight loss values during thermal degradation are summarized in Table I. Stoichiometric calculations according to these values led to the proposed fragmentation scheme (see Fig. 2). Lead carbazone complex $[Pb(C_{13}H_{11}N_4O)_2]$ dissociated at four 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 complex starts to dissociate at a temperature of 120°C, whereas that of carbazone complex starts to dissociate at about 100°C, indicating high stability of the lead–sulfur bond compared to that of the lead–oxygen bond. 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, ensuring their fragmentation to lead oxide and further to pure lead metal at the elevated temperature of 700°C.

## Polymer Yield Percentage, Molecular Weight, and Polydispersity

The percentage of conversion of MMA to PMMA samples in the presence of lead complexes varied from 80 to 95% compared to those prepared by pure thermal polymerization, which were about 85%. From Table II, it is obvious that the induction period increases with increasing the complex concentration, accompanied by molecular weight decrease and improvements of polydispersity data (Table III). This behavior indicates that

these complexes act as chain transfer. After 24 h the molecular weights of PMMA samples reached nearly half the value of those obtained by pure thermal polymerization.

## PMMA Structure and Crystallinity

The PMMA samples were confirmed structurally using FTIR (Fig. 3). No apparent change in the
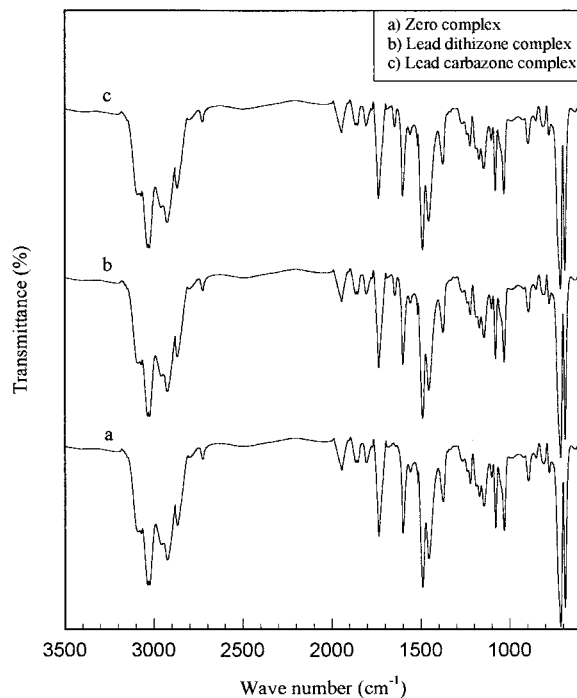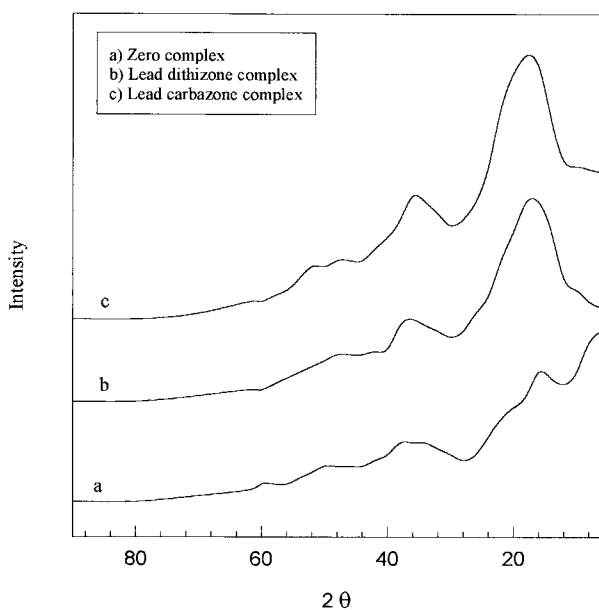


**Figure 3**   FTIR spectral analysis of PMMA in both the presence and the absence of lead complexes.

**Table IV   Variation of PMMA Tacticity with Lead Complex Concentrations**

| Sample | Isotacticity (%) | Heterotacticity (%) | Syndiotacticity (%) |
|---|---|---|---|
| Blank (zero complex) | 6.00 | 41.80 | 52.20 |
| Lead dithizone complex | | | |
| 0.05% | 6.70 | 38.10 | 55.20 |
| 0.10% | 6.10 | 41.80 | 53.10 |
| 0.15% | 5.70 | 41.00 | 53.30 |
| Lead carbazone complex | | | |
| 0.05% | 6.50 | 40.40 | 53.10 |
| 0.10% | 6.00 | 42.00 | 52.00 |
| 0.15% | 5.90 | 41.40 | 52.70 |

balance of either form of tacticity (i.e., isotactic, heterotactic, and syndiotactic) seemed to prevail, as illustrated from the IR spectra of all samples in both the presence and the absence of the lead complexes compared to model IR identification.[17] Attaining such tacticity was also confirmed from ^{1}H–NMR studies, where tacticity did not vary from blank PMMA samples (Table IV). Surprisingly, however, X-ray studies showed an improved order of polymer chains prepared in the presence of the lead complexes (Fig. 4). In the presence of lead complexes [Fig. 4(b), (c)] intensities at $2\theta = 17, 36$ for the lead dithizone complex and 18, 35 for the lead carbazone complex were increased compared to those prepared thermally in the absence of the complexes. The involvement of molecules of either lead complex in improving

the crystallinity of end product polymers indicates that leaching of such complex compounds would not be particularly accepted, and such complexes have become a well-bonded part of the PMMA molecules.

## Color Change and Reaction Mechanism

The molar absorptivity of lead dithizone complex in $CCl_4$ is $6.88 \times 10^4$ at $\lambda_{max} = 520$ nm, whereas

**Figure 4**  X-ray diffraction patterns for PMMA in both the presence and the absence of lead complexes.
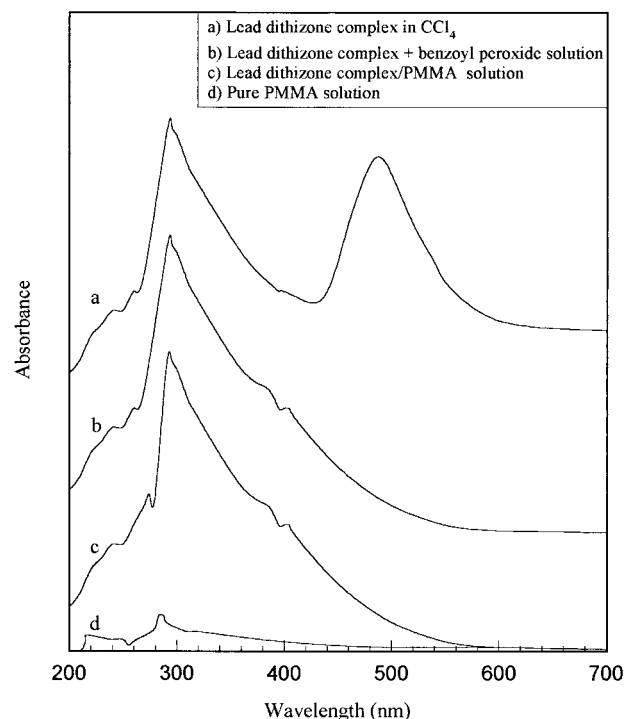
**Figure 5**  UV-visible spectral analysis for: (a) lead dithizone complex in $CCl_4$; (b) lead dithizonate complex in the presence of benzoyl peroxide; (c) PMMA solution in toluene prepared in the presence of lead dithizone complex; (d) pure PMMA solution in toluene prepared in the absence of lead dithizone complex.
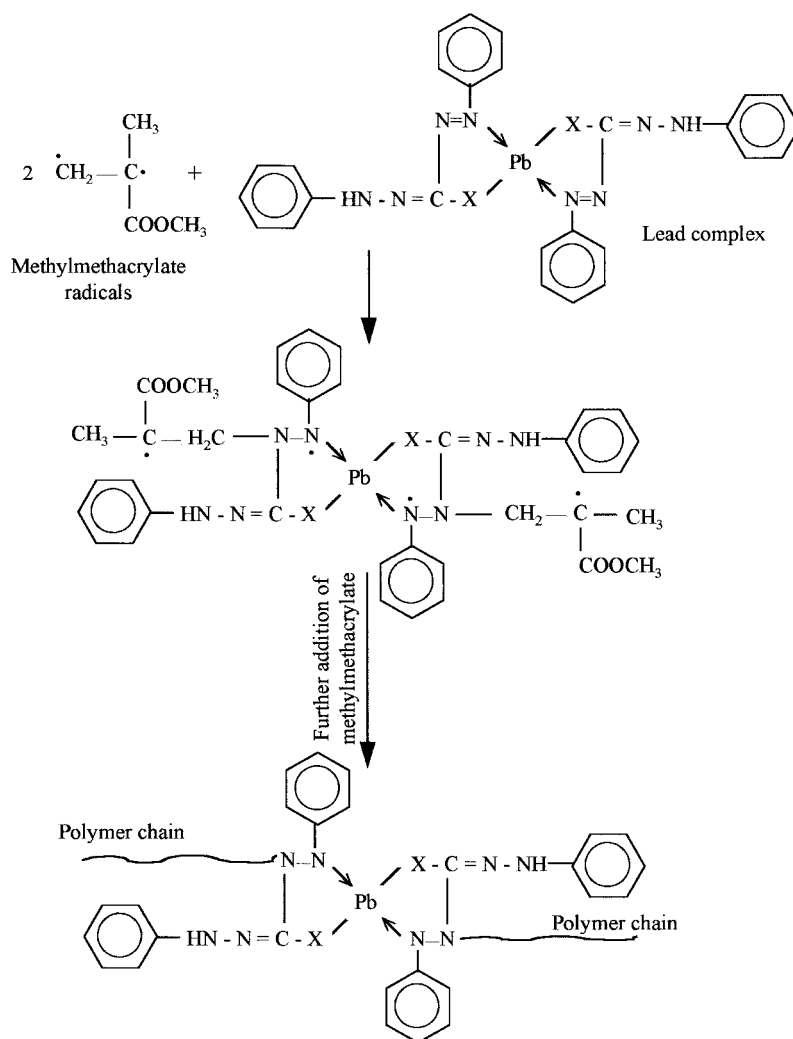
**Figure 6** Schematic reaction mechanism of MMA polymerization in the presence of lead complex.

that of lead carbazone complex is $7.20 \times 10^4$ (a = 0.35) at $\lambda_{max}$ = 508 nm. Lead dithizone complex in $CCl_4$, however, exhibits distinctive absorption bands at 596 and 296 nm [Fig. 5(a)]. PMMA samples prepared thermally showed no specific features of absorption resulting from the absence of any foreign or coloring materials [Fig. 5(d)]. However, PMMA samples prepared using lead dithizone complex as initiator still exhibited ultraviolet absorption bands at 296 nm, as shown in Figure 5(c), with a new shoulder at 405 nm attributed to color change. When lead dithizone complex is present in a reaction medium with liberated free radicals, such as those produced by benzoyl peroxide, the color changed from red to yellow with the disappearance of the band at 496 nm and the appearance of a new shoulder at 405

nm [Fig. 5(b)]. This color shift is attributed mainly to the formation of a peroxo-complex via azo group, whereas the new shoulder can be refereed to the formation of $\pi-\pi^*$ of C=N and C=O groups as a result of complex formation.[18] When observed during the polymerization of methylmethacrylate in the presence of lead dithizone complex, as illustrated, the same phenomenon of color change indicates the occurrence of a free-radical reaction.

Accordingly, the UV-visible absorption results and observations suggest the following:

1. Lead dithizonate is present in two tautomeric forms only when free radicals are present in the medium.
2. The polymerization process of methyl-

methacrylate, if made in the presence of lead dithizone complex, proceeds via a free-radical mechanism, accompanied by color change.

3. Color changes are observed as the polymerization process is completed as a result of the formation of an azo group of the present lead dithizone complex that is affected by the free radicals produced during the process.

A suggested reaction mechanism for the polymerization process of MMA in the presence of lead complex as initiator is illustrated in Figure 6.

## CONCLUSIONS

When present during the bulk polymerization of methylmethacrylate, lead dithizone and carbazone complexes proved as adequate initiators, at a conversion yield of 80–95%. They also function as indicators for the free-radical mechanism for the polymerization reaction, a mechanism of which was proposed. Lead dithizone and carbazone complexes proved to regulate polymer chain lengths through a chain-transfer mechanism. Such lead complexes also act as colorants for the polymer end product specified by tautomeric forms generated during the reaction. Polydispersity and uniform aggregation were observed in PMMA polymer samples, which might explain why polymers that contain such complexes would resist UV-irradiation, as reported earlier.[9] The formation of such two-arm metallo–PMMA complexes should function even more selectively in increasing the antidegradation polymer proper-

ties, a matter of ongoing investigation that will be reported in future communications.

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