Spectroscopic Study on Poly(Methyl Methacrylate) Doped with Metal Dithizonates

M. A. MOHARRAM,* A. A. SHABAKA, and M. G. KHAFAGI

Spectroscopy Lab. Physics Department, National Research Centre, Cairo, Egypt

SYNOPSIS

The IR and UV spectra of poly(methyl methacrylate) (PMMA) doped with metal dithizonate were investigated. Films of the doped samples were heated in air at various temperatures from 25 to 140°C for 2 h. Other films were also exposed to UV irradiation. The doped samples were treated with iodine. The experimental results provided strong evidence that certain weak reaction occurs between the dopants and the polymer, and the rate of reaction depends on the concentration of the dopant and the nature of the metal ions. It was found that heat treatment of the doped films induces considerable changes in the intensities of their IR bands. The magnitude of these changes depends also on the concentration and the nature of the metal ion. Moreover, the results proved that exposure of the doped films to UV irradiation has no effect on their absorption spectra. Furthermore, the treatment of the doped samples with iodine causes considerable changes in their UV absorption spectra.

INTRODUCTION

The studies of photoconductivity of charge transfer complexes performed hitherto fall into two groups. On the one hand there have been studies concerned with the mechanism of fluorescence quenching and dissociation process in solutions.[1,2] On the other hand, there have been investigations connected with the search for polymeric materials of relatively high photoelectric sensitivity and low dark current. These materials doped with acceptors forming charge transfer complexes are employed in the production of photosensitive films in electrophotography. The influence of the polymeric matrices on the mechanism of fluorescence quenching of the organic dyes has been investigated by a number of researchers.[3-5] Poly(methyl methacrylate) is among the polymeric materials that have been used as matrices for the organic dyes. It has also been accepted that metal dithizonates form an interesting class of photochromic complexes,[6] in addition ultraviolet, visible, and infrared spectroscopic technique were used for

the characterization of the structural properties of metal dithizonates.[7,8] These techniques have also been used for the investigation of the structure of PMMA.[9-12]

The present study is undertaken to apply ultraviolet and infrared spectroscopic techniques for the characterization of PMMA doped with metal dithizonates. The effect of heat, exposure to ultraviolet radiation, and doping with iodine on the spectral feature of the doped polymer will be investigated.

EXPERIMENTAL

The metal dithizonate complexes were prepared by the methods cited in the literature.[7,8] Solution of concentration 10^{-3} m/L of dithizone and its metal complexes in chloroform were prepared for UV measurements using a Beckman 5260 ultraviolet spectrophotometer. The solution of PMMA in chloroform at 10% (w/w) was homogenized for 1 h at 110°C. Solutions of dithizone (1, 3, 6, and 9 mL) at its metal complexes were then thoroughly mixed with 25 mL of the polymer solution. For the infrared measurements thin films of the mixtures several
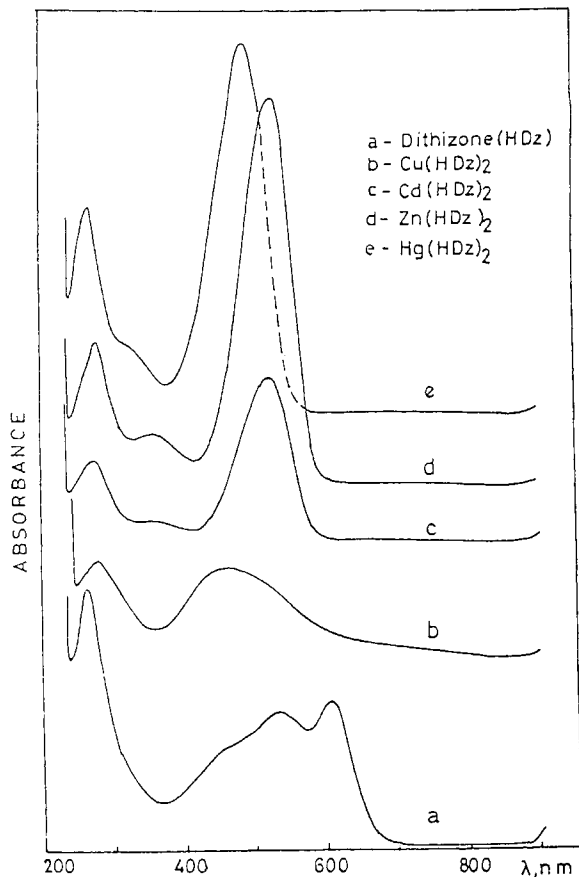
Figure 1 Electronic absorption spectra of dithizone and its metal complexes in chloroform with concentration ratio (1 : 25).
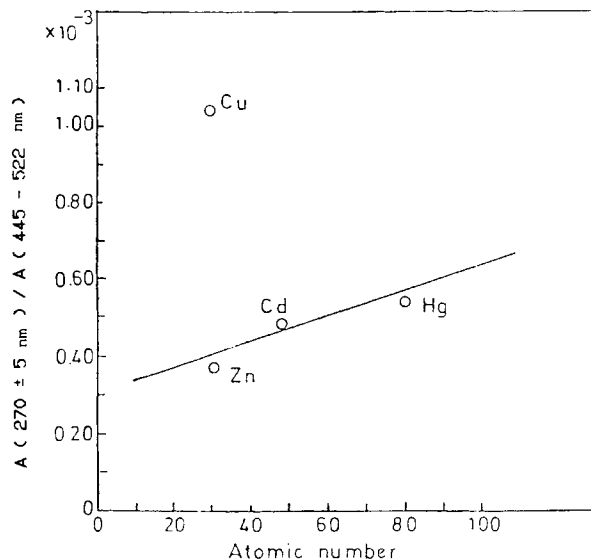

Figure 2 Relation between the obtained absorbance ratio and atomic number.

RESULTS AND DISCUSSION

The electronic absorption spectra of dithizone in chloroform as a solvent and its metal complexes are represented in Figure 1. As seen from Figure 1, the spectrum of dithizone shows four peaks at 608, 520, 448, and 265 nm. The absorption band at 608 disappears from the spectra of metal dithizonates, and an additional weak band appears in the spectra of Zn–Cd and Hg dithizonates at 360 and 320 nm, re-
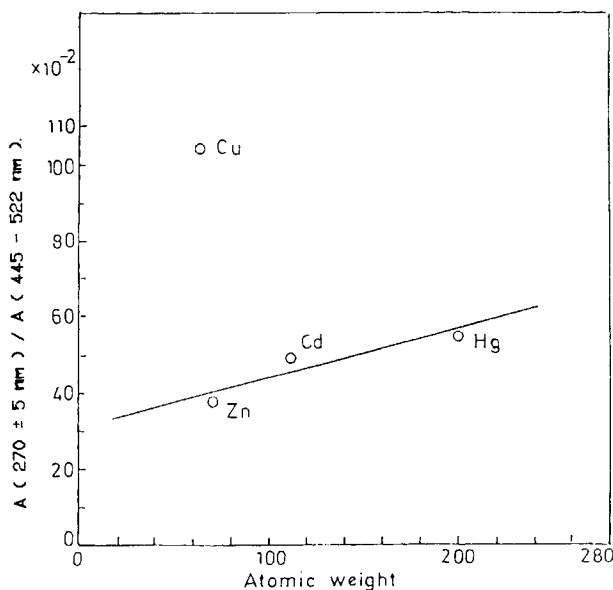
microns thick were prepared by evaporation of solvent from these solutions at room temperature on KBr disks. IR measurements were carried out on a Beckman 4250 IR spectrophotometer. The obtained absorbancies of the infrared absorption bands are the averages of three replicate runs. The accuracy of the measured values was found to be 4%. Other thick films for UV measurements were prepared by casting the solution on glass plates.

Table I   The Absorbance Ratio A (270 ± 5 nm)/ A(445–522 nm) for Dithizone and Its Metal Complexes in Chloroform as a Solvent

	Ratio	$\dfrac{\text{A (at } 270 \pm 5)}{\text{A (at } 445 - 522)}$
Dz	1.92	2.61
Cu		1.04
Zn		0.37
Cd		0.49
Hg		0.55

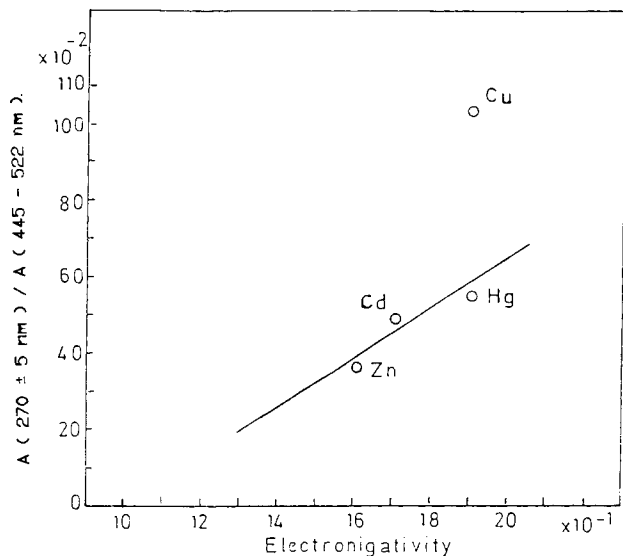**Figure 3** Relation between the obtained absorbance ratio and atomic weight.

Figure 4 Relation between the obtained absorbance ratio and electronegativity.

spectively. However, careful examination of the spectra of metal dithizonates reveals that the complex formation results in profound changes in the position and intensities of the absorption bands of dithizone.

The ratio of the absorbances of the band at 270 ± 5 nm and that of the band at 445–522 nm A(270 ± 5)/A(445–520) was determined. The determined values are given in Table I, which indicates that this ratio varies according to the nature of metal ion. The highest ratio is found in $Cu(HDZ)_2$ while the lowest one is found in $Zn(HDZ)_2$. But, in general, this ratio decreases as a result of complex formation.

The ratio A 270 ± 5/A 455–520 nm is plotted against the atomic number, atomic weight, electronegativity, and ionic radius of metal ion in Figures 2 to 5, respectively. It is apparent from Figures 2 to 5 that the absorbances ratio increases linearly with increasing atomic number, atomic weight, electronegativity, and the ionic radius of the metal ions; except for $Cu(HDZ)_2$, this relation deviates from linearity. This deviation can be attributed to the Jan Teller distortion of divalent Cu structure.

In the present study, PMMA was doped with different concentrations of dithizone and its metal complexes $Cu(HDZ)_2$, $Zn(HDZ)_2$, $Cd(HDZ)_2$, and $Hg(HDZ)_2$. The UV and visible spectra of these samples together with the spectrum of a pure sample of PMMA are represented in Figure 6. Figure 6 indicates that PMMA without dopant displays an intense absorption peak at about 215 nm and a weak one at about 285 nm. No absorption bands are observed above 300 nm. Careful examination of the spectra of the doped films reveals that the absorption band appearing in the spectra of $Cu(HDZ)_2$, $Zn(HDZ)_2$, $Cd(HDZ)_2$, and $Hg(HDZ)_2$ at 445, 522, 520, and 486 nm, respectively, is shifted to lower wavelength at 440, 520, 515, and 485 nm as a result of doping. According to this shift, one can come to the conclusion that certain reaction occurs between the dopants and PMMA.

The samples under investigation were then heated at various temperatures in air for 2 h. The spectra of the heat-treated films are illustrated in Figure 7. It can be easily seen from this figure that heat treatment of the film of dithizone-doped PMMA over the temperature range 25–140°C causes
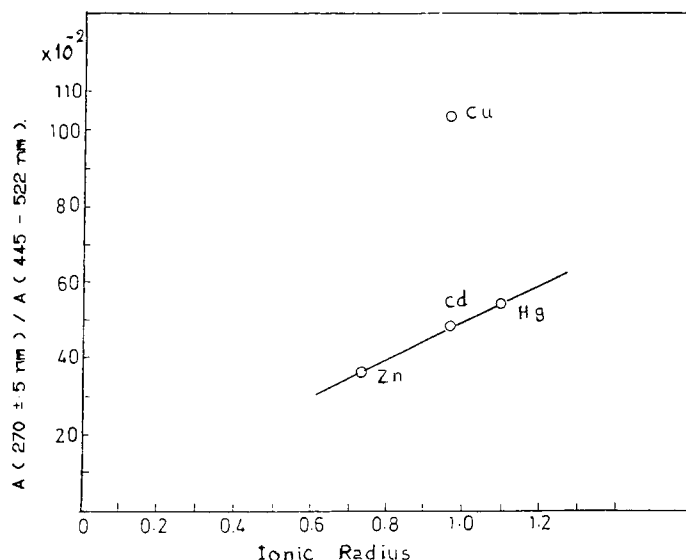

Figure 5 Relation between the obtained absorbance ratio and ionic radius.
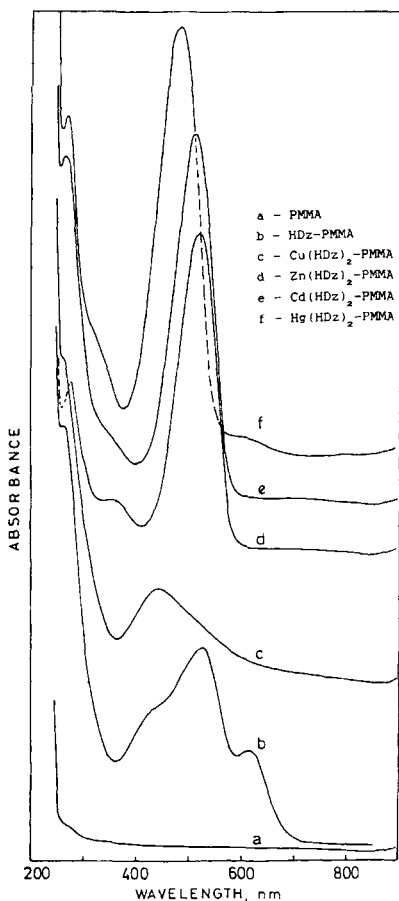
Figure 6 Electronic adsorption spectra of PMMA and PMMA doped with dithizone and metal dithizonate (9 mol/ratio).

remarkable changes in the intensities of the most evident absorption bands appearing at 608 and 448 nm. It is clear that heating of this film above 120°C results in the disappearance of these bands.

The ratio (R) of the absorbances of the band after and before heating for the same film was taken as a measure of the relative rate of change of the absorbance. The R values are plotted against temperature in Figure 8. The characteristic features of this relation for dithizone-doped PMMA are initial remarkable increase, followed by slight decrease, and followed by final sharp decrease. In the cases of samples doped with Hg($HDZ)_2$ and Zn($HDZ)_2$ the rate of change increases with increasing temperature up to 120°C and then decreases with elevating the temperature up to 140°C. In case of Cd($HDZ)_2$-doped PMMA the rate increases with increasing the temperature up to 100°C and then decreases with raising the temperature above 100°C. Based on the relationship between the relative rate of change of the absorbances and the temperature, one can sug-
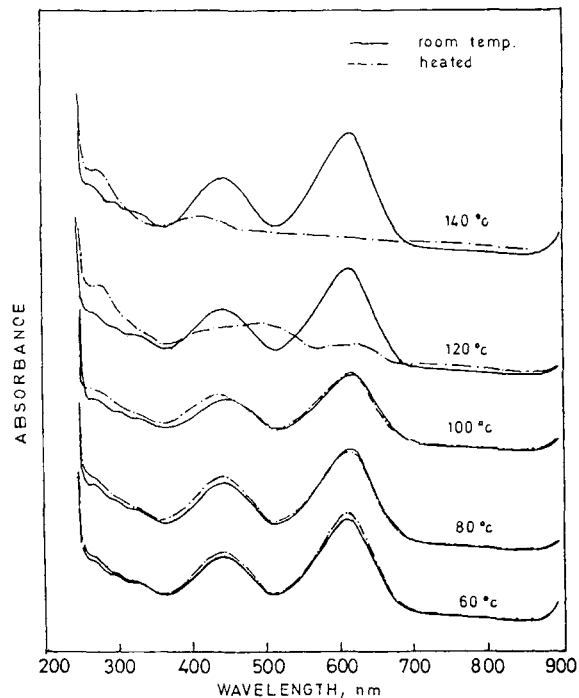

Figure 7 Electronic absorption spectra of HDZ–PMMA heated for 2 h at various temperatures.

gest that the thermal behavior of the dopped PMMA depends on the nature of metal ions.

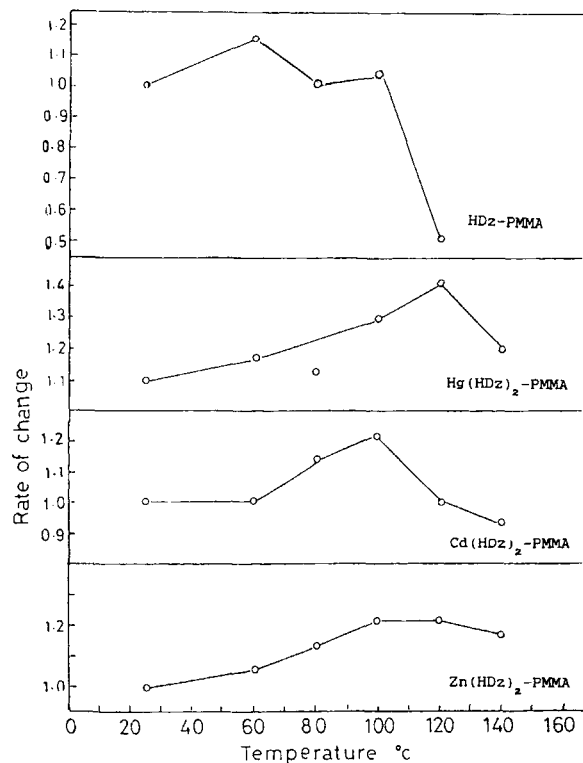Films of PMMA doped with dithizone and its

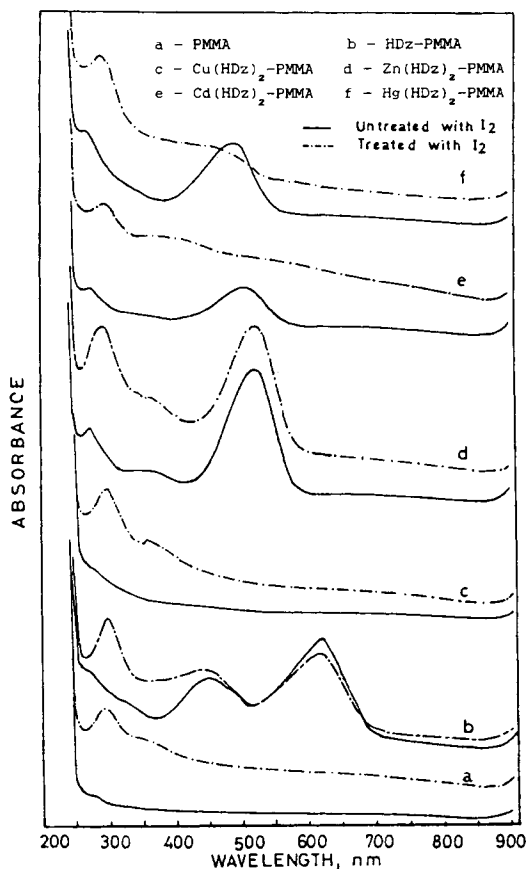**Figure 8** Relative rate of change against temperature.

Figure 9 Electronic absorption spectra of PMMA doped with dithizone and metal dithizonate before and after treatment with iodine.

metal complexes were then exposed to UV irradiation in a dark room for 15, 30, 60, 90, and 180 min and for 22 h. Analysis of the spectra showed that exposure of these films produces no significant changes in their spectra. Only, the bands of the spectra of the films doped with $Zn(HDZ)_2$, $Cd(HDZ)_2$, and $Hg(HDZ)_2$ displayed slight increases upon exposure for 90 min. Also the absorption bands of the sample doped with $Cu(HDZ)_2$ assumed slight increase after exposure for 15 min.

The doped samples of PMMA were then treated with iodine. The films were impregnated in a solution of iodine in acetone (1 g of iodine in 100 mL of acetone). As seen from Figure 9, the spectra of iodine-treated samples exhibit an absorption band at 280 nm due to the absorption of iodine. In general, it appears that the treatment with iodine causes remarkable decreases in the intensities of the absorption bands of dithizone and its metal complexes. The profound decreases are observed in the spectra of $Cd(HDZ)_2$ and $Hg(HDZ)_2$. The spectrum of the former sample shows no absorption bands corre-

sponding to $Cd(HDZ)_2$ while that of the latter shows only a very weak band due to the absorption of $Hg(HDZ)_2$.

The iodine-treated films of PMMA doped with dithizone and its metal (Zn, Hg) complexes were then exposed to UV irradiation for various period, viz. 30, 60, and 120 min. Analysis of the spectra of these samples showed that exposure of these samples produces slight changes in intensities of their absorption bands (see Fig. 10). Because these changes are very weak, it appears premature to draw definite conclusions about the effect of UV irradiation on the absorption bands of iodine-treated samples.

From the foregoing data it can be concluded that a certain weak reaction occurs between the dopant (HDZ) and its metal complexes and the base (PMMA). The dopants are sensitive to the effect of temperature and are not sensitive to the effect of UV irradiation. The iodine treatment causes considerable changes in the absorption bands of the dopants.

The infrared spectra of dithizone and metal dithizonate doped PMMA were recorded and are shown in Figure 11. These figures indicate that the resultant combined spectra do not show that the absorption frequencies of PMMA have changed in
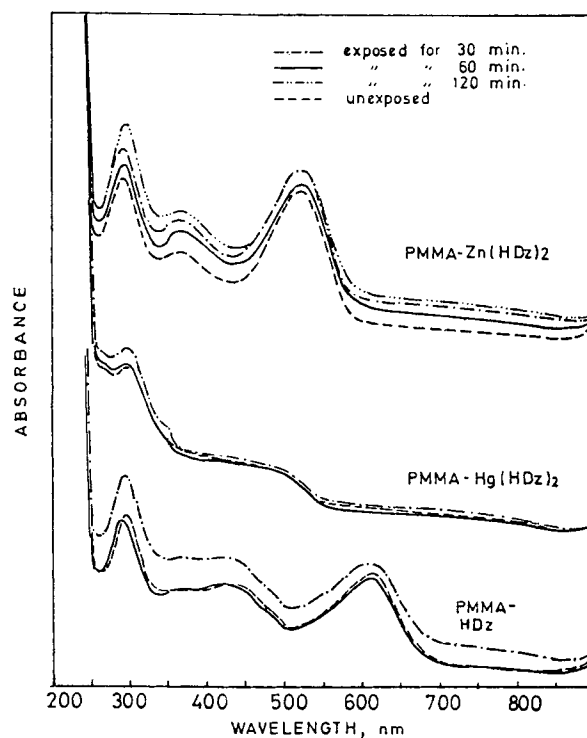

Figure 10 Electronic absorption spectra of PMMA doped with dithizone and metal dithizonates treated with iodine and exposed to UV radiation for various periods of time.
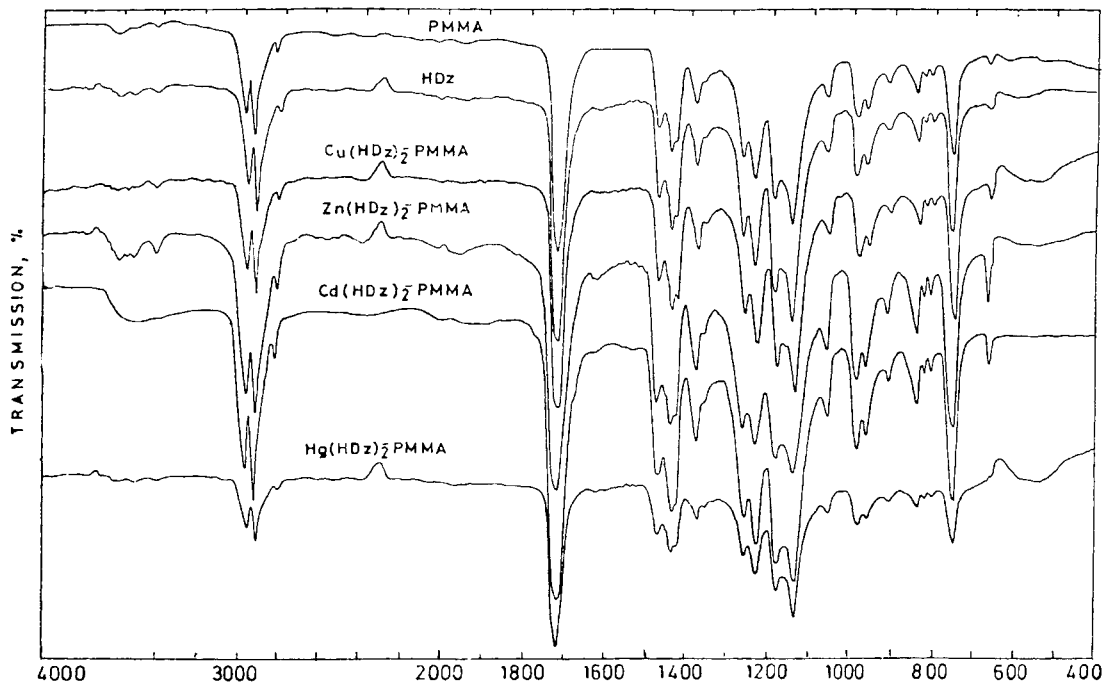
Figure 11   IR spectra of PMMA and PMMA doped with dithizone and metal dithizonate.

process. It is not possible to show directly that a wavelength shift or an intensity change of the stretching C=O band or any other band occur since such changes can occur as a result of two unresolved

components. However, the changes are likely to be accompanied by a change in absorption intensity, and hence the ratio of the absorbances of the C=O band at 1730 cm^{-1} and that of the C—H stretching
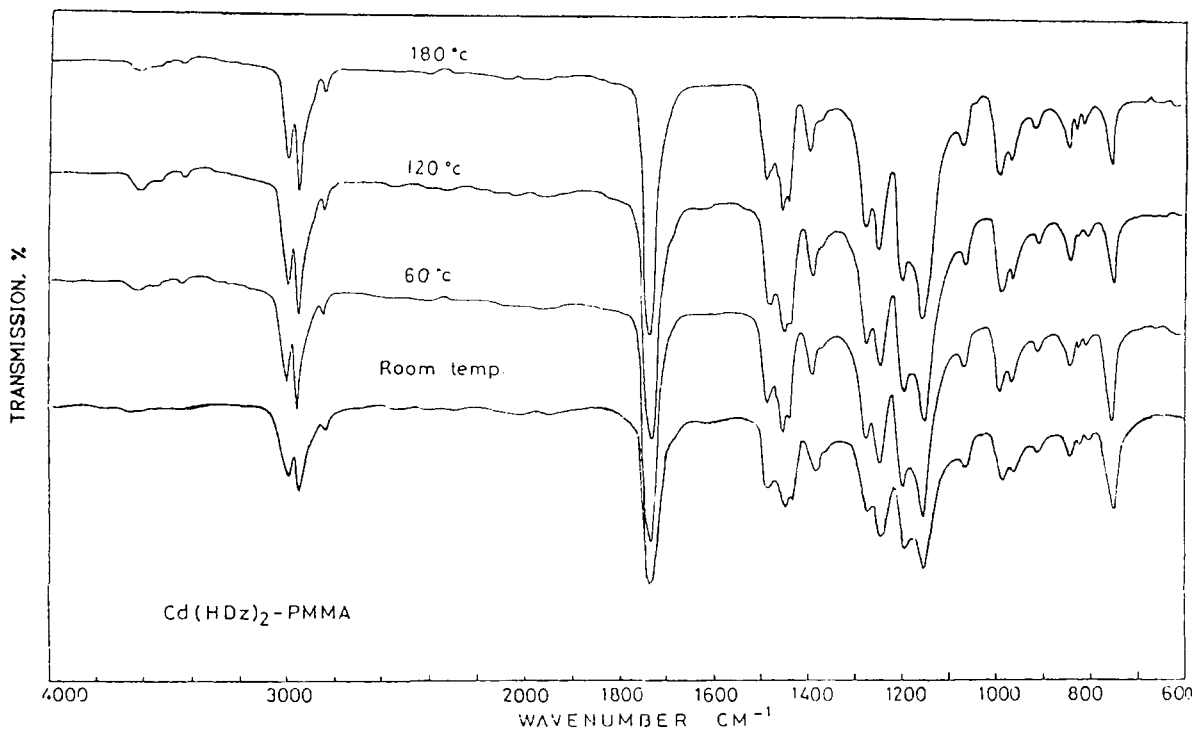

Figure 12   Spectra of heated samples of Cd(HDZ)$_2$ PMMA.

Table II   Effect of Temperature and Concentration of Dopent on the Ratio A 1730/A 2942

| Temperature (°C) | Dopant Concentration (mL) | | | | | | | | | | |
| | PMMA | HDZ | | $Zn(HDZ)_2$ | | $Cu(HDZ)_2$ | | $Cd(HDZ)_2$ | | $Hg(HDZ)_2$ | |
	0	3	9	3	9	3	9	3	9	3	9
25	2.39	2.63	2.49	1.52	3.38	3.28	3.09	1.49	1.93	3.36	1.76
60	2.60	2.96	2.65	—	—	3.44	2.40	1.76	2.36	3.35	2.63
80	—	—	—	2.30	3.73	—	—	—	—	—	—
120	2.00	1.83	2.31	1.79	3.35	2.67	2.32	1.40	2.11	2.32	2.50
160	—	2.18	2.72	—	—	—	—	—	—	—	—
180	2.46	—	—	1.98	4.53	3.17	2.67	1.88	2.57	2.95	3.05

band at 2942 cm^{-1} were measured by using the base-line method. Baselines were drawn between 3300 and 2660 cm^{-1} and from 1870 to 1550 cm^{-1} across the 2942 and 1730 cm^{-1} bands, respectively. The determined ratios are given in Table II.

Table II provides strong evidence that doping of PMMA with dithizone or with its metal complexes causes considerable changes in the absorbances ratio A 1730/A 2942, and these changes depend on the concentration of dopants and the nature of metal ions. This experimental result proves that the dop-ants react with PMMA, and it is in good agreement with the results obtained by ultraviolet investigation.

The samples were then heat treated at different
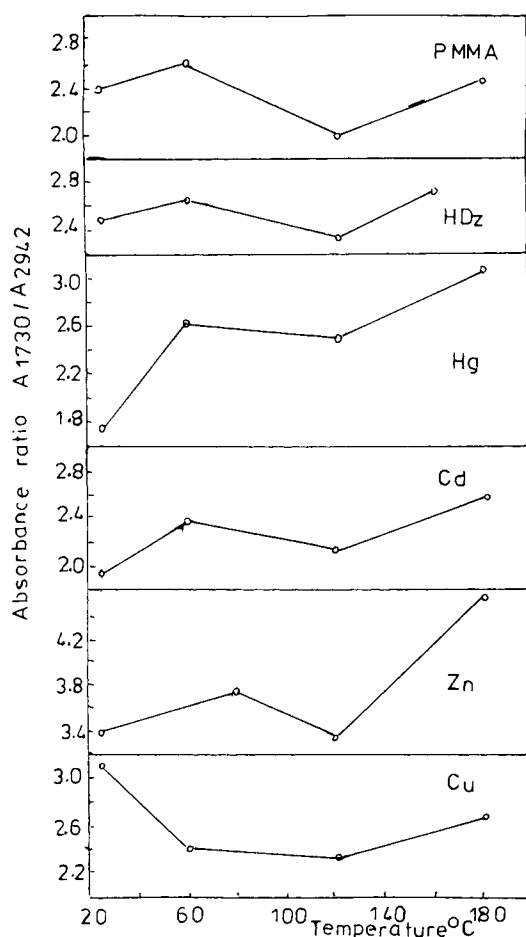
Figure 13 Relation between the temperature and ab-sorbance ratio A 1730/A 2942.
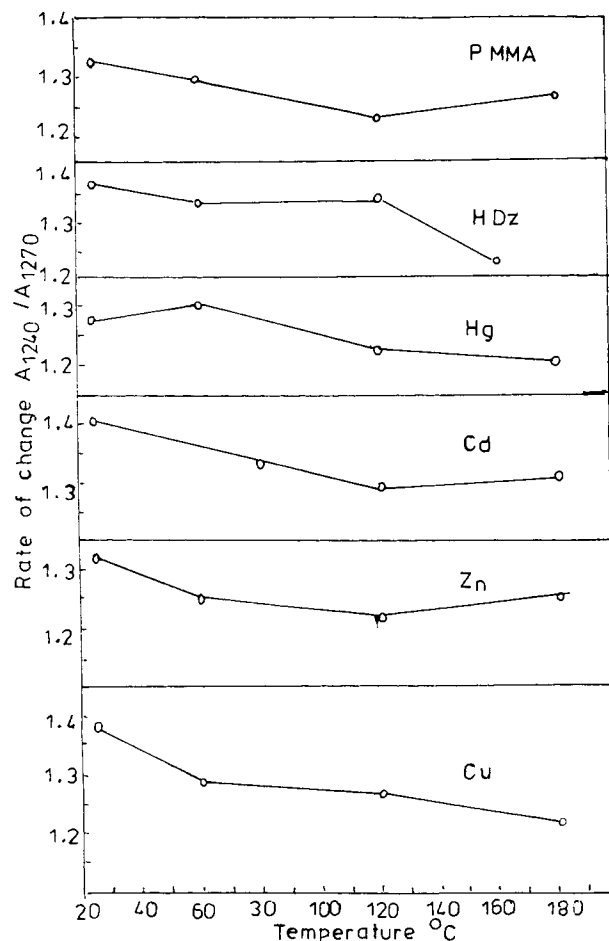
Figure 14 Relation between the temperature and ab-sorbance ratio A 1240/A 1270.

temperatures up to 180°C. Figure 12 shows examples of the spectra of the heated samples. The absorbances ratio of the heated samples are given in Table II. It is apparent from Table II that the absorbance ratio is affected by the temperature, and the temperature-induced changes depend on the nature of the metal ions of the metal complexes.

Figure 13 shows the relation between the temperature and the absorbances ratio A 1730/A 2942. It is clear from Table II and Figure 13 that for pure and doped PMMA the absorbance ratio assumes a minimum value at 120°C, and this value varies from sample to sample and depends on the concentration and the nature of metallic ion of the dopant. Moreover, heat treatment of the samples causes considerable changes in the absorbance ratio A 1730/A 2942 and the induced changes depend on the temperature of heating. The minimum value that occurs at 120°C may be because the glass transition of PMMA takes place around this temperature. Indeed, the variation of the absorbance ratio can at least suggest that certain reactions take place between the dopants and the ester group of PMMA.

Additional information concerning the reaction between the dopants and the ester groups of the base can be obtained from the determination of the ratio of the absorbances of the bands at 1240 and 1270 cm^{-1}. These two bands are assigned as C—C—O stretching vibration coupled with C—O. Havrhiak and Roman[13] used this ratio for obtaining some information concerning the structural properties of PMMA.

The determined values of the ratio A 1240/A 1270 are plotted against the temperature for the samples doped with concentration 9 as shown in Figure 14. It can be easily seen from this figure that this ratio depends on the nature of metal ions and on the temperature of heating. This result confirms the previous finding that the dopants react with the ester groups of PMMA.

The above-mentioned consideration can lead to the conclusion that the dopants react with the ester groups of PMMA, and this reaction depends on the concentration of dopants and the nature of the metal ions. Also the thermal treatment of the doped samples induces considerable changes in the structure of the films. The induced changes depend also on the concentration and the nature of metals.

REFERENCES

1. H. Masuhara, M. Shimada, N. T. Sujino, and M. Mataga, *Bull. Chem. Soc. Japan,* **44,** 3310 (1971).
2. H. Irie, S. Tomimoto, and K. Hayashi, *J. Phys. Chem.,* **76,** 1419 (1972).
3. N. Geacintov, G. Oster, and T. Cassen, *J. Optic. Soc. Am.,* **58,** 1217 (1968).
4. A. Degorski and M. Kryszeuski, *J. Chem. Soc. Trans. Faraday,* **71,** 1513 (1974).
5. J. M. Drake, M. L. Lesiecki, J. Sansregret, and W. R. Thomas, *Appl. Optic.,* **21,** 245 (1982).
6. Pupko and Pelkis, *Zhur. Obschei Khim,* **27,** 2190 (1957).
7. L. S. Meriwether, E. C. Breitner, and N. B. Colthup, *J. Am. Chem. Soc.,* **81**(20), 4441 (1965).
8. L. S. Meriwether, E. C. Breither, and C. L. Sloan, *J. Am. Chem. Soc.,* **87**(20), 449 (1965).
9. H. Geosling, A. Adamson, and A. Gutierrez, *Inor. Chimica, Acta,* **29,** 279 (1978).
10. M. Nagai, *J. Appl. Polym. Sci.,* **7,** 1697 (1963).
11. J. Spevacek, B. Schneider, J. Dybal, J. Stokr, J. Balbrian, and Z. Pelzbauer, *J. Polym. Sci.,* **22,** 617 (1984).
12. J. Dybal, J. Spevacek, and B. Schneider, *J. Polym. Sci.,* **24,** 657 (1986).
13. S. Havriliak, Jr. and N. Roman, *Polymer,* **7,** 387 (1966).