# Structural and Optical Properties of Iodine-Doped PMMA Film

## D. S. KELKAR, A. P. GADRE

Institute of Science, Department of Physics, Madam Cama Road, Bombay 400032, India

Received 2 May 1997; accepted 30 April 1998

ABSTRACT: Poly(methyl methacrylate) (PMMA) film was cast from solution in benzene (4% W/V). Various samples of iodine-doped PMMA films were prepared by adding different amount of iodine, namely, 0.5, 1, 2, and 8% (w/w), respectively, to PMMA solution in benzene. The structures of pristine and doped PMMA were investigated using analysis of their infrared spectra and wide-angle X-ray diffraction analysis. The refractive index of pristine PMMA is almost equal to that of glass. Changes in the refractive index of various doped PMMA samples have been determined from their reflectance and transmission spectra in ultraviolet–visible range. It has been observed that the refractive index increases at low concentrations of doping, and it is maximum for 1% iodine doping. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1627–1631, 1998

**Key words:** poly(methyl methacrylate); infrared spectrum; X-ray diffraction, refractive index

# **INTRODUCTION**

The infrared (IR) characteristics of poly(methyl methacrylate) (PMMA) have been the subject of several investigations.<sup>1-3</sup> The object of most of these investigations was to describe the dependence of infrared characteristics in terms of the stereoregular nature of polymer chain. Infrared spectra were used by Nagai<sup>2</sup> to measure the tacticity of the polymer. After doping a polymer, it is possible that a complex is formed due to the dopant molecule. The formation of complex is reflected in the (IR) spectrum of the doped polymer. Using the IR spectrum of iodine-doped PMMA at various concentration, the complex formation has been studied. PMMA is reported to be an amorphous polymer<sup>4</sup>; as a result, its X-ray diffraction scan shows an amorphous halo at  $2\theta = 7^{\circ}$  and 20.5°. It has been reported that iodine doping of nylon-6 changes its structure from monoclinic ( $\alpha$ )

to hexagonal  $(\gamma)$ .<sup>5</sup> It was therefore thought to be interesting to study the structural changes in PMMA after doping with iodine.

PMMA has received great attention due to its optical properties and its possible use in nonlinear optics. Different properties of PMMA have been studied after doping by various dopants, and dielectric properties of malechite green-doped PMMA<sup>6</sup> and optical biostability in azobenzinedoped PMMA have been reported.<sup>7</sup> Franke has also studied the refractive index pattern in cosinmethylene blue-doped PMMA<sup>8</sup> film. Iodine has been used as a dopant in many other polymers like nylon-6, polyaniline, and polyacetylene. In the present work, iodine has been used in different proportions as a dopant for PMMA. While studing the optical properties of PMMA, the refractive index measurements were carried out using reflectance and transmission spectra,<sup>9</sup> and the optical constant n was calculated using the different equations at wavelength  $\lambda = 400$  nm as well as  $\lambda = 450$  nm. The changes in refractive index with concentrations of doping have been discussed.

Correspondence to: D. S. Kelkar.

Journal of Applied Polymer Science, Vol. 70, 1627-1631 (1998)

<sup>© 1998</sup> John Wiley & Sons, Inc. CCC 0021-8995/98/081627-05



Figure 1 Infrared spectra of (a) undoped film, (b) 1% iodine-doped PMMA, and (c) 2.5% iodine-doped PMMA.

# **EXPERIMENTAL**

The PMMA used in the experiment (Aldrich chemical Co., USA) had an average molecular weight 120,000. PMMA and was dissolved in benzene (as supplied from S.D. Fine Chemicals, Boiser, India (AR grade; 4% w/v), and its film was cast on a clean glass plate at room temperature. To prepare iodine-doped films of PMMA, a measured weight of iodine crystals (resublimed) was added to the solution of PMMA in benzene. The mixture was stirred, and the film was cast on a clean glass plate at room temperature. Thus, various samples of iodine-doped PMMA film were prepared by adding different amount of iodine, namely, 0.5, 1, 2.5, 5, and 8% (w/w) to the PMMA solution in benzene. These concentrations in terms of molar ratios of iodine to PMMA are 5 : 1, 10 : 1, 25 : 1, 50 : 1, and 80 : 1, respectively, for the above samples. The films have thickness about 25  $\mu$ m.

The IR spectra of PMMA films were recorded in the frequency range of 400 to 4000 cm<sup>-1</sup> on a Perkin–Elmer Fourier transform infrared (FTIR) instrument 1600, with normal slit in the 10-min scan mode. Wide-angle X-ray diffraction (WAXD) scans were recorded on JEOL JDX-8030 X-ray diffractometer. Nickel-filtered copper radiation was incident on the sample, which was scanned at 1°/min in reflection mode over a range of  $2\theta$  from 5 to 35°. The reflectance and transmission spectra were recorded on the ultraviolet–visible (UV–vis) spectrophotometer Milton Roy, Color Scan-II for the refractive index measurements.

## **RESULTS AND DISCUSSIONS**

## Analysis of Infrared Spectra

Figure 1 shows IR spectra for pure, 1% and 2.5% iodine-doped PMMA samples.

Nagai<sup>2</sup> has reported that the appearance of the band at 1067.3 cm<sup>-1</sup> is indicative of either atactic or syndiotactic nature of PMMA.<sup>2</sup> The comparison of IR spectra of pristine PMMA and that for (0.5, 2.5, 5.0 and 8.0%) iodine doped films reveal that the changes in various bands are not appreciable. The IR spectra of 0.5, 5, and 8% iodine-doped PMMA films are found to be similar to Fig. 1(c) (2.5% iodine-doped); hence, they are not reproduced here.

However, the IR spectra of 1% iodine-doped PMMA film shows a remarkable shift in 1730 $cm^{-1}$  band. Changes are also observed at the bands appearing at 1150 and 1242  $\text{cm}^{-1}$ . These bands are guite sharp for pure and other doped samples, but the bands appear to merge by sharp fall in the intensity of the absorption at 1225  $cm^{-1}$  for 1% doped sample. The band appearing at about 2835  $\text{cm}^{-1}$  for 1% iodine-doped sample is more prominent, which exists as only a shoulder in case of other samples. The band at  $1730 \text{ cm}^{-1}$ is reported to be due to the C=O group.<sup>2</sup> The changes appearing in this band for 1% iodinedoped sample points out towards the possibility of iodine molecule getting attached to C=O group in the side chain of PMMA molecule. It has also been observed that for 1% iodine-doped film, the bands at 1150 and 1242  $\text{cm}^{-1}$  show a broad nature. These bands are associated with skeletal streching coupled with C-H deformation vibration. These bands arise due to intermolecular interactions.<sup>2</sup> In case of the same sample, the band at  $2835 \text{ cm}^{-1}$  becomes more sharp and prominent. This band is the combination band associated with ester CH<sub>3</sub> group. From the observed changes in the above bands (1150, 1242, and 2835  $\text{cm}^{-1}$ ), together they indicate some change in the CH<sub>3</sub> group of the side chain structure. Thus, it may be possible that iodine molecule gets attached between C=O as well as the CH<sub>3</sub> group in the side chain of the PMMA molecule.

The attachment of iodine molecule to C=O and  $CH_3$  groups similarly must be taking place at a low concentration of doping also. However, for the low concentration, such changes are not observed. The reason for this may be that for a low concentration of doping, the number of iodine molecules that get attached is less, to be observable in the IR spectrum. At high concentration (more than 1%), the number of iodine molecules is so large that most of them have no place to be attached to the C=O or  $CH_3$  groups (All such sites are consumed up to a 1% iodine concentration.) Thus, the molecules get separated and deposited in between the side chain space, leaving the IR spectrum of iodine doped PMMA undisturbed.

#### Wide-Angle X-ray Defraction Analysis

Figure 2 shows the WAXD scans for undoped and 1 and 2.5% iodine-doped PMMA film. The X-ray scan of pure PMMA and 2.5% iodine-doped PMMA [Fig. 2(a) and (c)] show an amorphous nature with no sharp peaks and an amorphous



**Figure 2** X-ray diffraction scan of (a) undoped film, (b) 1% iodine-doped PMMA, and (c) 2.5% iodine-doped PMMA.

halo at  $2\theta = 23^{\circ}$ . For 1% iodine-doped PMMA [Fig. 2(b)], the amorphous halo at  $2\theta = 23^{\circ}$  disappears. For this sample, the peak appears at  $2\theta = 12^{\circ}$ . The X-ray diffraction (XRD) scans for 1% iodine-doped sample is quite different from that of pure or other doped samples. This suggests that some structural change in the molecular chain packing may be taking place. Analysis of the IR spectrum of 1% iodine-doped PMMA film also supports this suggestion.

Thus, the analysis of IR spectra and the WAXD analysis point towards some structural change taking place for the 1% iodine-doped sample.

## **Optical Properties**

The optical constant n (refractive index) was calculated from the transmittance and reflectance measurements carried out for the various samples.<sup>9</sup> Transmission and reflectance spectra in UV–vis range are shown in Figures 3 and 4, respectively.

It is well known that the absorption coefficient  $(\alpha)$  at a given wavelength is related to the transmission T (%) by the following relation<sup>9</sup>:

$$T(\lambda) = (1 - R)e^{-\alpha t} \tag{1}$$



Figure 3 Transmission spectra of (a) 0.5%, (b) 1%, and (c) 2.5% iodine-doped PMMA films.

where *t* is the thickness of the film and *R* is the corresponding reflectance at that wavelength  $\lambda$  in nm. Also, reflectance *R* is related to absorption coefficient  $-\alpha$  by another relation, as follows:

$$R = \gamma (1 + T \times e^{-\alpha t}) \tag{2}$$

where  $\gamma$  is the reflection coefficient.<sup>9</sup> From eqs. (1) and (2), we obtain

$$R = \gamma \left( 1 + \frac{T^2}{(1-R)} \right) \tag{3}$$

Here, we have assumed that the multiple reflection taking place in the interior of samples are negligibly small. From eq. (3), the value of  $\gamma$  was obtained for  $\lambda = 400$  and 450 nm. After substituting, the values of *R* (reflectance) and *T* (transmittance) were obtained from the respective spectra for different values of  $\lambda$  (wavelength). Similarly, since the thickness of the film *t* is known,  $\alpha$  was calculated using eq. (1) for  $\lambda = 400$  and = 450 nm, respectively. From these calculated values of  $\gamma$ and the corresponding values of  $\alpha$ , for a particular wavelength ( $\lambda$ ), the optical constant *n* may be determined using the following relations:

$$\gamma = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
 and  $\alpha = \frac{4\pi k}{\lambda}$ 

The values of refractive indices obtained for pure as well as iodine-doped PMMA films have been tabulated (Table I). From the table, it is obvious that the values of the refractive indices increase up to 1% concentration film, and it becomes maximum at 1% concentration for both



Figure 4 Reflectance spectra of (a) 0.5%, (b) 1%, and (c) 2.5% iodine-doped PMMA films.

Sample	$\lambda = 400 \text{ nm}$ Refractive Index $(n)$	$\lambda = 450 \text{ nm}$ Refractive Index (n)
0.5% Iodine-doped PMMA film	1.4982	1.5447
1% Iodine-doped PMMA film	2.1130	2.8015
2.5% Iodine-doped PMMA film	1.4959	1.6810
5% Iodine-doped PMMA film	1.4980	1.5271
8% Iodine-doped PMMA film	1.4962	1.5113

Table I Refractive Indices of Various Iodine-Doped PMMA Films at  $\lambda = 400$  and 450 nm

the wavelengths, that is, at  $\lambda = 400$  nm, as well as  $\lambda = 450$  nm.

## Discussion

To explain the change in the value of refractive index of PMMA, the mathematical method developed by Bahr and Pinto<sup>10</sup> (to fit their experimental data) has been used. According to the Lorimer<sup>11</sup> equation for refractive index of polymer solution,

$$\eta = \eta_0 + vc_p + ac_p^2 \tag{4}$$

where  $\eta$  is the refractive index of doped films,  $\eta_0$  is the refractive index of general solvent, *a* is second-order coefficient in eq. (4) [(g/mL)<sup>-2</sup>]; *v* is the incremental coefficient in eq. (4) [(g/mL)<sup>-2</sup>]; and  $c_p$  is polymer concentration (g/mL).

If chemically doped polymer is looked upon as a solid solution of the dopant and polymer, then the same theory developed by Bhar and Pinto<sup>10</sup> may be used to explain the changes in the refractive index of the doped film. In this case, then,  $\eta$  would be the refractive index of the doped film;  $\eta_0$ , the refractive index of the solvent, that is, the polymer PMMA;  $c_p$ , the concentration of iodine; and vand a, the coefficients that are linear functions of  $\eta_0$ , that is, the refractive index of PMMA. Thus, it may be easy to explain why the refractive index is more than that of pure PMMA after doping. The refractive index of the doped film is obtained after adding  $vc_p$  and  $ac_p^2$  to  $\eta_0$ , which is the refractive index of pure PMMA. The refractive index of the film must increase with the concentration of doping. However, it is found that the refractive index goes on, increasing only up to 1% concentration of doping. A further increase in dopant concentration reduces the value of the refractive index. This fall in the refractive index may be the result of collection of iodine particles within the PMMA

chain. It has already been observed that for the concentrations above 1%, that is, 2.5, 5, and 8%, the iodine remains uncomplexed, like in the form of undissolved particles. This uncomplexed iodine must be responsible in reducing the refractive index of the mixture.

# CONCLUSION

From the analysis of IR spectra and WAXD analysis of doped PMMA, it may be said that the structural changes take place after doping with iodine as a result of complex formation of iodine with the carbonyl group of PMMA. It has also been observed that the refractive index changes after doping. Thus, it may be concluded that the structural changes in PMMA after doping are responsible for changing the refractive index of PMMA.

# REFERENCES

- S. Havriliak Jr. and M. Roman, *Polymer*, 7, 387 (1996).
- 2. H. Nagai, J. Appl. Polym. Sci., 7, 1697 (1963).
- T. R. Manley and C. G. Martin, *Polymer*, **12**, 524 (1971).
- R. P. Kusy, J. Polym. Sci., Chem. Ed., 14, 1527 (1976).
- 5. I. Abu Isa, J. Polym. Sci., A1, 199 (1971).
- P. K. Khare, M. S. Gaur, and R. Singh, *Ind. J. Phy.*, 68A, 545 (1994).
- Z. Zhang, Y. T. Chow, E. Y. B. Pun, and Y. E. Peixian, Jpn. J. Appl. Phy., 34, 122 (1995).
- 8. H. Franke, Polymer, 28, 659 (1987).
- A. Abdelghany, S. M. Yossel, S. N. Elsayed, and A. H. Abou El Ela, *Ind. J. Pure Appl. Phys.*, **32**, 789 (1994).
- O. Bhar and J. C. Pinto, J. Appl. Polym. Sci., 42, 2795 (1991).
- 11. J. W. Lorimer, Polymer, 13, 274 (1972).