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Studies on the Photodegradation of Poly(Methyl Methacrylate)

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ABSTRACT

Although poly(methyl methacrylate), PMMA, is
known to degrade when exposed to ultraviolet radiation,
studies at wavelengths other than 253.7 nm have not
been done. The lack of knowledge about the mechanism
of degradation of PMMA at wavelengths other than 253.7
nm hinders efforts to develop short-term test methods
for predicting the long-term performance of PMMA in
applications in which it is exposed to sunlight. This
study was performed to determine the effect of ultraviolet
radiation on PMMA and to identify mechanisms of degradation
induced by the radiation.

Thin films of PMMA of two different molecular
weights were irradiated with radiation nominally of 253.7 nm
and 300 nm. The irradiations were conducted in air and
under vacuum. Exposure at 253.7 nm caused a rapid decrease
in molecular mass and loss of a small amount of volatile
products, which is a characteristic of random chain scission.
The quantum yield was greater in air than in vacuum. Changes
in the molecular mass and the glass transition temperature
as well as weight loss data indicating that wavelengths
bands at greater than 253.7 nm also cause degradation. The
data further indicate that the degradation at the longer
wavelengths may not be completely random scission.

ACKNOWLEDGMENT

1. INTRODUCTION

1.1 Background

Poly(methyl methacrylate), PMMA, is an important polymer in the building industry as well as in other industries. Typical applications are in architectural coatings and in glazing material of high impact resistance including cover plates in solar energy systems. When exposed to sunlight, PMMA may undergo changes which alter its properties. For this reason, it is essential to study its long-term performance and to understand the mechanisms by which its properties change.

The ultraviolet (UV) component is the most damaging part of sunlight because of its high energy. The photon energy associated with it is of the order of 0.3 to 0.4 MJ, which is in the range of carbon-carbon single bond energy. UV radiation may cause carbon-carbon bonds to break, resulting in a scission of the polymer chain. Other bonds, e.g. carbon-oxygen, carbon-hydrogen, may also break. The most characteristic feature of random scission of a polymer chain is a rapid decrease in the molecular mass. Molecular mass changes, accompanied by changes in the physical and mechanical properties of a polymer, may cause a reduction in its mechanical properties and its ability to perform adequately in some applications.

Previous studies of the effect of UV irradiation on PMMA have been carried out using 253.7 nm radiation sources from low and medium pressure mercury (Hg) lamps. The techniques typically used to detect degradation include determination of molecular mass change, quantum yield of scission, and UV, IR and ESR (electron spin resonance) spectra. From the above measurements, the rate of degradation can be determined.

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The change in molecular mass is most often determined from viscosity measurements [1-8]. The photodegradation of PMMA by 253.7 nm radiation results in a rapid decrease in the viscosity average molecular weight and the formation of small amounts of volatile products. Fox et al. [7] assumed that the number of scissions occurring in the PMMA chain was proportional to the number of quanta absorbed by the chain and they identified the proportionality constant as the quantum yield of chain scission. They reported a quantum yield of random scission of 4×10^{-2} per absorbed quantum at a pressure of 2.7 m Pa $(2 \times 10^{-5}$ mm Hg) of air. A hundred fold increase in the air pressure did not affect the resulting quantum yield while, at atmospheric pressure, the quantum yield was 1.7×10^{-2}. Charlesby et al. [6] reported a quantum yield of 4×10^{-3} for the photolysis of thin films of PMMA in air and in nitrogen.

PMMA has a low absorption at 253.7 nm and the incident radiation can penetrate into the polymer sample. Irradiation of the polymer cause the appearance of two new absorption bands in the UV region; one at 240 nm, which has been assigned to conjugated unsaturation, and another at 285 nm, which is probably due to carbonyl chromophores [7,9,10].

The IR spectrum of PMMA changes little on irradiation with 253.7 nm radiation [7,9,10]. Only a broadening of the carbonyl band at 5.71 μm (1750 cm^{-1}) and the formation of new bands at 6.19 μm (1615 cm^{-1}) and 6.01 μm (1640 cm^{-1}) were observed. The latter two bands are attributed to olefinic unsaturation [7,9,10].

Electron spin resonance (ESR) spectra of PMMA irradiated with UV (253.7 nm) and γ-rays are almost identical [11]. This indicates that the same

free radicals are formed during both kinds of irradiations. The following four

free radicals have been reported [6, 11, 12]:

a)
$$CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}} \cdot$$

b)
$$CH_2 - \overset{\overset{\displaystyle \cdot CH_2}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{CH}}$$

c) $\cdot CH_3$

d) $H - \overset{\displaystyle \cdot}{C} = 0$
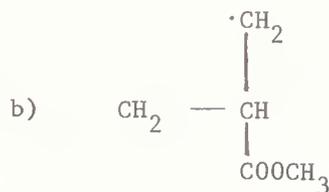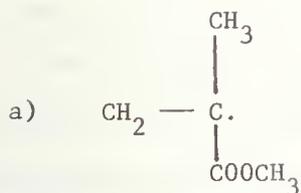
Keto and Nishoka [13] determined that the half life of methyl radicals was

1.5 hours for both UV and γ radiated PMMA samples at 77 K. Charlesby et al.

[14,15] compared the results obtained from UV and γ irradiation of PMMA at

different temperatures. At high temperature (above 170 °C), depolymerization

was much less with γ radiation than with UV. This finding was interpreted as

indicating that UV radiation at high temperature is selectively absorbed at

unsaturated chain ends resulting in depolymerization [15].

The photodegradation of PMMA in 2-chloroethanol solution has been investigated

[15] as a function of irradiation time, polymer concentration, temperature

(25-159 °C) and intensity of the incident beam. The investigators reported

that the random chain scission initial reaction was dependent on polymer

concentration. They also added that, at elevated temperatures (54° to 159

°C), an absorption peak at 224 nm increased in intensity with irradiation

time. This increase was shown to be a measure of the amount of monomer formed during photolysis. Charlesby and his coworkers claimed that, under the experimental conditions, thermal degradation was negligible. Only monomer has been detected from the unzipping mechanism as a result of the thermal degradation of PMMA.

Unzipping is a continuous release of monomer from the end of the polymer chain once the scission of the chain has started. The decrease in the molecular weight due to unzipping is slow in contrast to that resulting from photodegradation. The kinetic chain lengths of PMMA, determined from the average number of monomer molecules per main chain scission, were less than 14 at 25°C but increased to 312 at a temperature of 159°C. Photolysis of PMMA in benzene solution has also been investigated by Kardash and Krongeuz [17] and Charlesby and Thomas [6]. The latter authors found the quantum yield for random scission of PMMA in benzene solution to be independent of polymer concentration.

The photodegradation of PMMA may result in a random scission of the polymer chain backbone by radical process [1-3,7,18-25]. The major reactions thought to occur simultaneously are:

1) Random homolysis scission of main chain carbon-carbon bonds:

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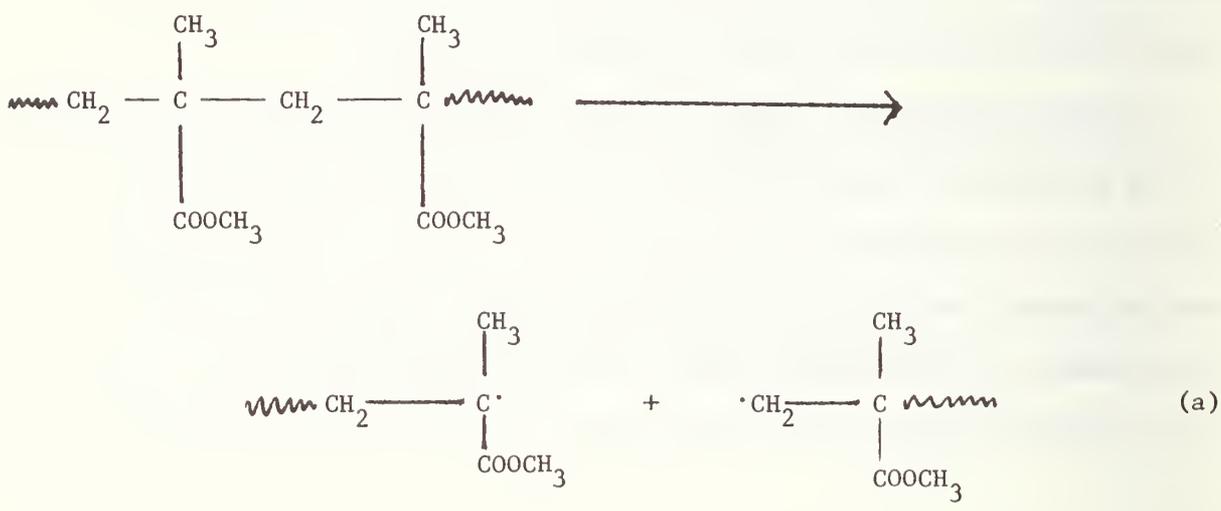
2) Photolysis of ester side group in three different ways:

$$\text{www CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\bullet}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad + \quad {}^{\bullet}COOCH_3 \qquad (b)$$

$$\text{www CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad \xrightarrow{\ h\nu\ } \quad$$

(c)

$$\text{www CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle {}^{\bullet}CO}{|}}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad + \quad {}^{\bullet}OCH_3 \qquad (c)$$

$$\text{www CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COO^{\bullet}}{|}}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad + \quad {}^{\bullet}CH_3 \qquad (d)$$
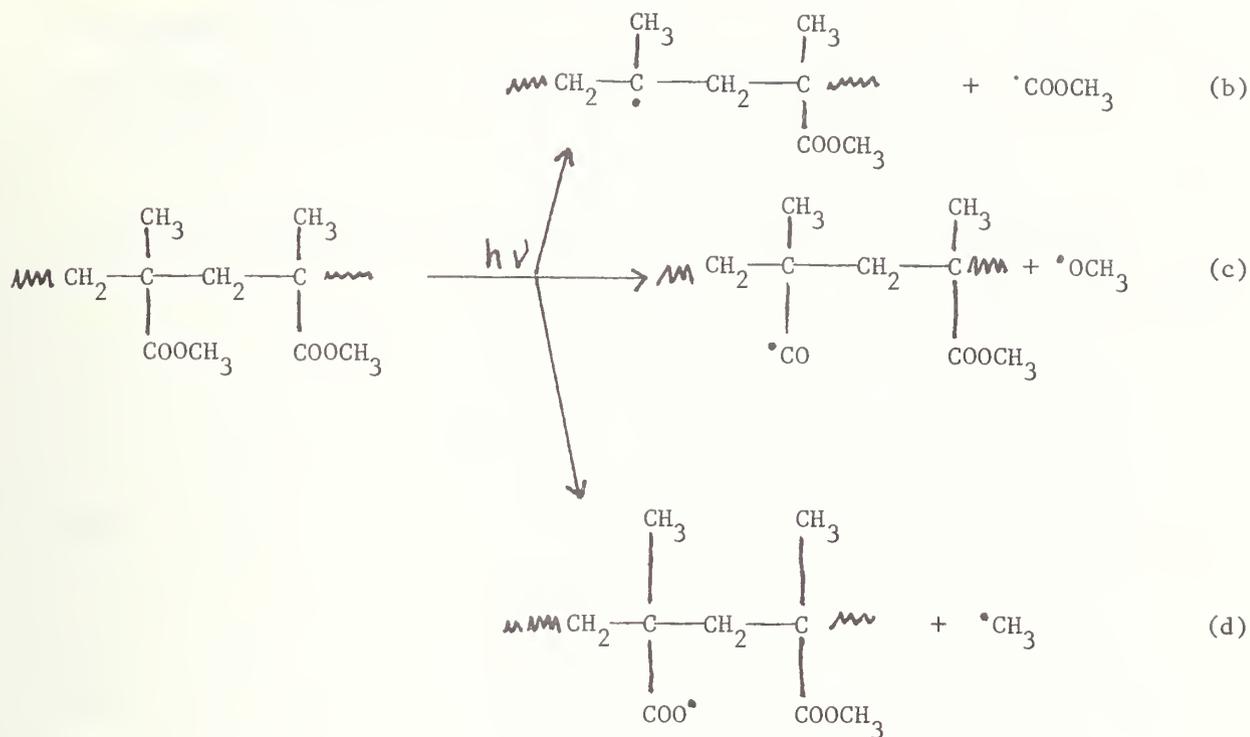
3) Photodissociation of the methyl side chain group:

$$\text{www CH}_2\text{—}\overset{\overset{\displaystyle CH_3\ C}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad \xrightarrow{\ h\nu\ }$$

$$\text{www CH}_2\text{—}\overset{\bullet}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{—CH}_2\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOCH_3}{|}}{C}}\text{www} \quad + \quad {}^{\bullet}CH_3 \qquad (e)$$

5
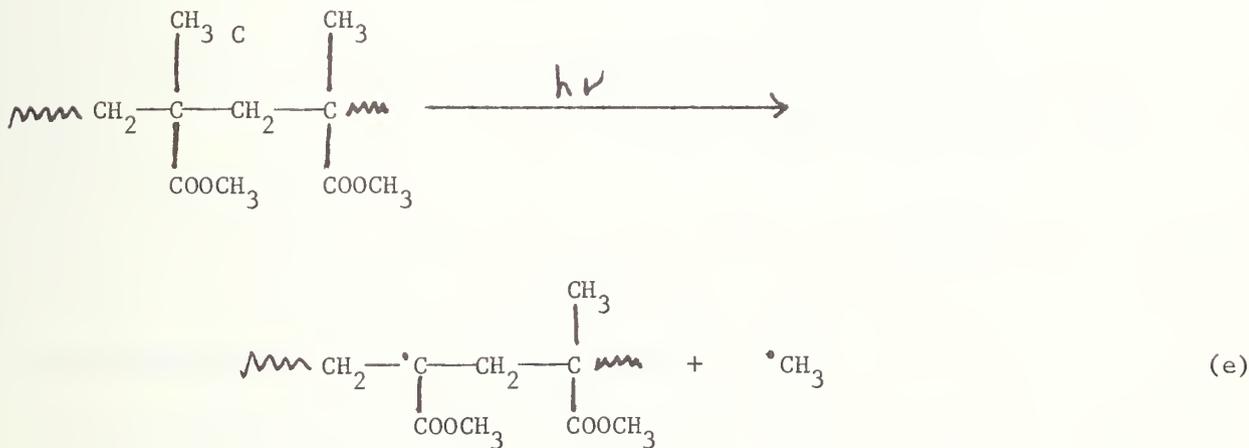
The main volatile products of the photolysis of PMMA in vacuum are methyl formate, methanol and methyl methacrylate with quantum yields of 0.14, 0.48 and 0.20, respectively. In air, additional products include methane, hydrogen, carbon monoxide and carbon dioxide [7].

Monomer methyl methacrylate can originate in at least three ways during PMMA degradation:

1) End chain depolymerization (unzipping)

$$
\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\sim\sim\sim CH_2 - C - CH_2 - }} \overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C^{\bullet}}} \longrightarrow
$$

$$
\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{\sim\sim\sim CH_2 - C^{\bullet}}} \quad + \quad \overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{CH_2 = C}}
$$
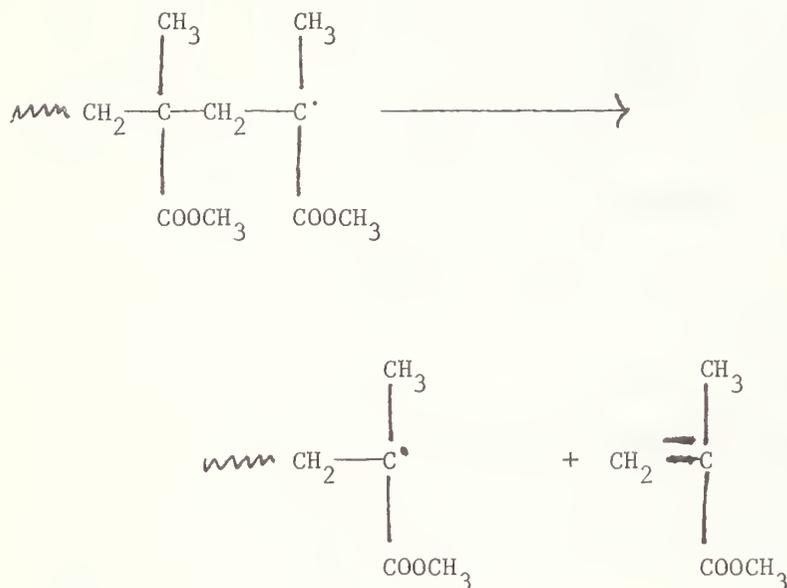
2) Trapped residual monomer from the initial polymerization

3) Random thermal degradation

Monomer methyl methacrylate formed during UV irradiation is mainly due to depolymerization after photolytic scission of the main chain as in (a). A maximum zip length of about 5 monomer units per scission at 25°C was indicated [7]. With increasing irradiation temperature (up to 160°C), a minimum kinetic

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chain length of 220 monomer units per scission [1,2] and 312 at 159°C was reported by Jellink [16]. No cross linking has been reported when PMMA is irradiated as a film or in solution.

In contrast, the dominant product of thermal degradation of PMMA is monomer which is liberated in high yield at 250°C. PMMA degradation was the first polymer degradation reaction to be investigated in detail [27,28]. The principal features were revealed by a combination of molecular weight and rate of monomer formation measurements. The molecular mass changes which occur during thermal degradation in PMMA of various molecular mass are illustrated in Figure (1). Grassie [29] explained the fact that the molecular mass of low molecular mass polymer does not change during degradation by demonstrating that complete molecules are lost from the polymer. This suggested to him a reaction mechanism which is the reverse of a radical polymerization. The initiation process in this reaction involves scission of the molecule to produce radicals, which unzip to produce monomer. The entire process, called depolymerization, may be represented generally as the following:

Initiation
$$M_n \longrightarrow M_j^{\cdot} + M_{n-j}^{\cdot}$$
$$M_n \longrightarrow M_{n-1}^{\cdot} + M \cdot$$

Depropagation
$$M_{n-1}^{\cdot} \longrightarrow M_{n-2}^{\cdot} + M$$

Transfer
$$M_i^{\cdot} \longrightarrow M_{i-z}^{\cdot} + M_z$$
$$M_j^{\cdot} \longrightarrow M_{j-z} + M_z$$

$$M_j^{\cdot} + M_n \longrightarrow M_j + M_n^{\cdot}$$

Termination
$$M_j^{\cdot} + M_i^{\cdot} \longrightarrow M_j + M_i \quad \text{or } M_{i+j}$$
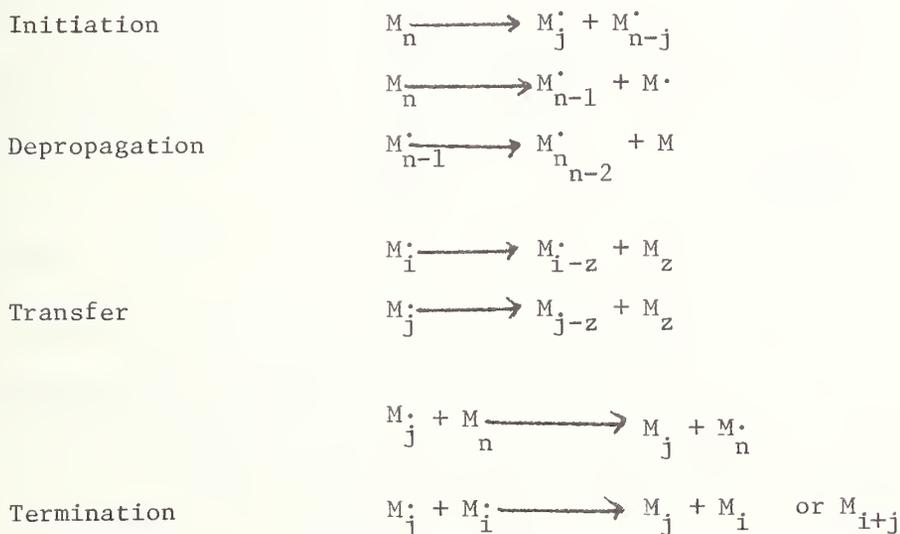
where

      n: is the kinetic chain length of the starting material

M_i, M_j, M_{i+j} represent dead polymer molecules (have no radical)

$M_i^\cdot, M_j^\cdot, M_2^\cdot$, etc.   are chain radicals

    Grassie [28] reported the formation of the monomer through the unzipping process as follows:

$$
\sim\sim\sim CH_2 \!-\! \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \!-\! CH_2 \!-\! \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\cdot}} \longrightarrow
$$

$$
\sim\sim\sim CH_2 \!-\! \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C^\cdot}} \quad + \quad CH_2 \!=\! \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}
$$

8
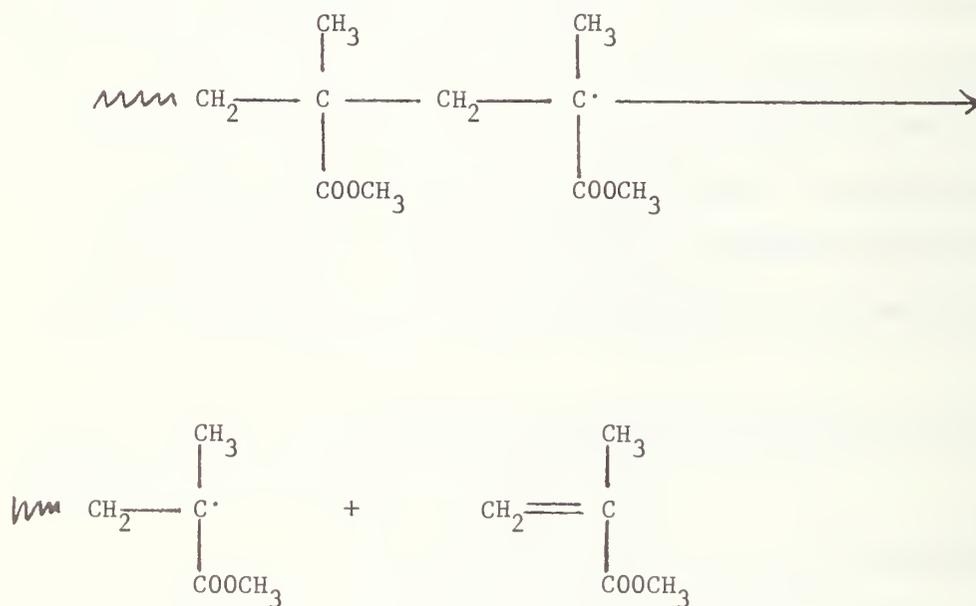
Grassi [29] stated that the unchanging molecular mass in low molecular mass PMMA suggested that there was a high probability that the depropagation would reach the end of the molecule before the termination process, which would stabilize the radicals, could intervene. Otherwise, the average molecular mass would decrease with volatilization. As the initial molecular mass of PMMA is increased, the probability that the degrading radicals will be stabilized by mutual interaction of pairs, as in radical polymerization, is increased. The resulting residual low molecular weight material causes the decrease in molecular weight to occur progressively earlier in the reaction as the molecular weight of the initial PMMA is increased.

The photodegradation of PMMA has been studied using a 253.7 nm source, while the spectrum of natural sunlight at the earth's surface cuts off at about 292 nm. However, when PMMA is exposed to sunlight for long periods of time, it is known to degrade. For this reason, there is a need to study the effects of UV and visible radiation on the polymer degradation. Such studies should emphasize identification of the mechanisms of the degradation under these conditions. The results of photodegradation studies, combined with those of simulated natural weathering of PMMA, are urgently needed to permit prediction of long-term performance in building applications by short-term testing.

1.2 Scope

Because of the wide use of PMMA in coating and other building material this study was proposed to have the following three objectives:

1. To investigate the effect of different bands of UV and visible light as well as combination of these bands on the photodegradation of PMMA.

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2. To study the mechanism of the photodegradation caused by the individual or combination bands.

3. To investigate the effect of simulated natural weathering on the photodegradation of PMMA using a xenon-arc accelerated weathering machine.

2. MATERIAL AND APPARATUS

2.1 Polymer

Test samples of poly(methylmethacrylate) were provided by the Research Laboratory Division of the (Rohm and Haas Co.)[*] Two different molecular weight products were provided. The weight average molecular weight of the first was stated to be 190,000 while that for the second was 240,000. The two polymers have been designated PMMA I and II, respectively. They were reported by the supplier to contain UV stabilizer and ca. 1% residual monomer and to have 75% syndiotactic character.

2.2 Light Source

The photochemical reactor was a Rayonet Model RPR-100,[*] obtained from the Southern New England Ultra-violet Company, Middletown, Connecticut. The apparatus is shown in Figures 2 and 3. It consists of a sheet metal housing and a bank of 16 tubular UV lamps. Within the housing, the 285 mm length lamps were mounted vertically around a circle of 235 mm diameter. Surrounding the cyclinder of lamps is a polished cylindrical reflector, 390 mm in height

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[*]DISCLAIMER: Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

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and 260 mm in diameter. A fan in the base of the reactor blows air through the irradiation space to cool the material being irradiated. The interior of the reactor is shown in Figure 3.

Three sets of lamps are available commercially, with spectral distribution peaking at 253.7 nm, 300 nm and 350 nm. The spectral distribution of the three sets of lamps were measured and shown in Figures 4 through 6, respectively.

2.3 Actinometry

Actinometry was performed during the exposure tests to measure the amount of radiation the samples received. These measurements were necessary to permit comparison of the fluxes for different lamps and to permit a determination of the quantum efficiency of the degradation. The procedure employed was that of McLaughlin et al. [30,31]. In this method, the colorless pararosaniline cyanide becomes deeply colored upon irradiation with ultraviolet radiation. Its quantum efficiency is 0.96 mol/photon up to 340 nm [30,31].

2.4 Molecular Mass Measurement

The molecular mass was measured by gel permeation chromatography using a Water Associates chromatograph. The columns used were packed with Microstyrogel. Six columns was used, four of pore size .01 mm, one each of .1 and 10 μm. The diluent used, tetrahydrofuran, was degassed daily during the measurements. The differential refractometer was a Waters Associates model R401. The resulting chromatographic data were analysed by computer to give number and weight average molecular mass.

2.5   Thermal Mechanical Analyzer (TMA)

The glass transition temperature for the original and the degraded polymer was measured using a Dupont Model No. 941 Thermal Mechanical Analyzer. Figures 7 and 8 show the TMA apparatus used.

3.   TEST PROCEDURES

3.1 Polymer Preparation

3.1.1 Purification of PMMA

The polymer samples were dissolved in methylene chloride (analytical grade) by boiling the methylene chloride solution until complete dissolution was obtained. The solution was then cooled to about 10°C, and the PMMA precipitated by adding cold methyl alcohol (also at about 10°C). The precipitated solid was filtered under suction. This process was done twice to insure the removal of most of the residual monomer and all the UV absorber originally present the UV spectra of the treated polymer show no presence of the UV absorber.

3.1.2 Film Casting

After purification, the polymer was dissolved in methylene chloride and cast on polished black glass using a draw down blade. The blade, made of cold-rolled steel, had a wide U-shape. The filmflow opening of the one edge used had a clearance of 254 micrometer and a width of 139.7 mm. After evaporation of the solvent, the film was released by immersing the glass plate in water. The middle part of the film was used in the tests to insure a uniform thickness of 20 ± 5 micrometer.

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3.1.3 Heat Treatment

Each film was heated to 100°C for 8-16 hours, then at 80°C under vacuum for 16 hours. This treatment removed the residual solvent and any stresses developed in the film during casting.

3.2 Irradiation of the Polymer.

After the PMMA film was freed from the residual solvent, it was weighed and attached with clips to a quartz microscope slide (7.5 x 2.5 mm) The microscope slide with the film was mounted vertically inside a quartz tube in the center of the photochemical reactor. The polymer samples were irradiated, using either the 253.7 or 300 nm lamps, in air and under a vacuum of .07 K Pa (0.5 mm mercury) for various intervals of time. After a few exposure trials the polymer film was exposed to the 253.7 nm lamps for 1/2, 1, 1-1/2, 2, 3, 4, 5, 6 and 8 hour intervals, and to the 300 nm lamps for 2, 4, 8, 16 24, 32, 48 and 64 hour intervals.

3.3 Actinometry

A solution of pararosaniline cyanide of 1.136 mg/m^3 gm/ml concentration in isopropyl alcohol (spectro grade) was used for actinometry. Its molar extinction coefficient was measured at its absorption maximum (549nm) to be 1.31×10^7 mol^{-1} m^{-1}. McLaughlin [30] determined the value to be 1.39×10^7 mol^{-1} m^{-1}.

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In order to duplicate exposure conditions of the PMMA irradiations, actinometry was performed as follows:

A quartz cell of 1 mm path length was filled with pararosaniline cyanide (0.35 cm^3 capacity) and placed vertically in the center of the reactor inside a quartz tube and irradiated for certain intervals of time (e.g. 3,5 and 7 seconds). The absorbance (A) at 549 nm was measured using a spectrophotometer. By measuring the absorbance the intensity of the UV light received by the pararosaniline cyanide per second (I), could be calculated, and the intensity of irradiation absorbed by the PMMA sample (Ia) could be calculated.

3.4   Molecular Mass Measurements

The original and degraded PMMA were dissolved in tetrahydrofuran to give concentrations ranging between 0.25 and 1.0 % by mass. The solution was filtered twice under pressure through Teflon filters. A 100-200 nm^3 sample of the solution was then injected into the chromatograph. The diluent (tetrahydrofuran) was degassed daily during the measurements by filtering through a fretted glass suction funnel. The resulting chromatographic data were analyzed by computer to give number and mass average molecular masses.

3.5 Glass Transition Temperature (Tg)

The glass transition temperature, Tg, for the original and degraded PMMA was measured using a thermal mechanical analyzer (TMA) (Figures 6 and 7). The round tip probe was used, and the instrument conditions were

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as follows:

Temperature scale	0 to 200°C
Probe displacement	.14 μm/mm
Loading on Tray	10 g
Heating Rate	10°C/min.

Three measurements were made for each sample and the average calculated to
the nearest degree.

3.6 UV and IR Spectra

The transmissions of the original and degraded PMMA films were scanned
from 210 - 360 nm using a Beckman DK1 spectrophotometer. The IR spectra
were measured for the PMMA films using a Perkin Elmer Model 467 spectro-
photometer between 2-5 and 40 μm.

3.7 Volitile Loss of Polymer

The percentage of mass loss (as volatile products) during the
irradiation of PMMA I and II was determined by weighing , to 10^{-5} gram,
the film before and after exposure.

4.   RESULTS AND DISCUSSION

4.1 Molecular Mass Changes

The results of the changes in mass average and number average
molecular mass for the original and degraded PMMA I and II during

irradiation with 253.7 nm lamps in air and under vacuum are shown in
Tables 1 through 4. (The mass average molecular mass was in consistant
with that reported by the supplier.) Changes during irradiation with 300 nm
lamps are shown in Tables 5 through 8. It is clear from these results that
the effect of irradiation is a rapid decrease in the molecular mass of both
PMMA I and II. The 253.7 lamps are more effective in inducing degradation
than the 300 nm lamps; i.e. for the same amount of degradation it took a
longer time of exposure using the 300 nm lamps.

A comparison of the changes in the number average molecular mass
with the intensity of the absorbed irradiation between PMMA I and II
is shown in Figures 9 through 12. The graphs illustrate that the behavior
of PMMA I and II were similar although they were originally different in
molecular mass. Another observation is that the rate of degradation
under all the different conditions of exposures (air or vacuum also with
253.7 nm and 300 nm lamps) is greater initially, than during the latter
stages.

The quantum yield for chain scission ($\emptyset_{cs}$) calculated from the
molecular mass changes during irradiation, is tabulated in Tables 1 through 8
according to the following equation:

$$\emptyset_{cs} = \frac{\ell \ N \left[\overline{M}_{n_0} \middle/ \overline{M}_{np} - 1 \right]}{\overline{M}_{n_0} \cdot I_a \ t}$$

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where

ℓ =   is the density of PMMA mg/m^3

N =   Avogadro's number

$\bar{M}_{n_o}$ and $\bar{M}_{n_p}$ =   original and degraded number average molecular mass

         respectively.

I_a =   intensity of absorbed radiation (photon/cm^3sec)

t =   time of exposure in seconds.

For PMMA irradiated with 253.7 nm lamps, the quantum yield was calculated to be between 3.0×10^{-2} and 4.55×10^{-2} in air and between 2.45×10^{-2} and 3.46×10^{-2} in vacuum. For PMMA irradiated with 300 nm lamps, the quantum yield was between 0.64×10^{-2} and 1.21×10^{-2} in air and between 0.51×10^{-2} and 1.06×10^{-2} in vacuum.

Two important observations follow from the above results. First, the rate of degradation in air is higher than in vacuum for PMMA I and II, which is opposite to the finding of Fox et al. [7]. The higher quantum yield in air may be attributed to the result of simultaneous photooxidation and photo-degradation. Secondly, at the same intensity the rate of degradation for PMMA irradiated with the 300 nm lamps is much less than that observed with the 253.7 nm lamps (about one fourth). It is apparent from Figs. 4 and 5 that the intensity of the 253.7 nm output from the 300 nm lamps was determined

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to be one tenth of that from the 253.7 nm lamps. It can be concluded that the irradiation by the bands longer than 253.7 nm (311, 365, 436 nm), which are of greater intensity in the 300 nm lamps, can play an important role in the photodegradation of PMMA.

4.2 Glass Transition Temperature

The effect of irradiation on the glass transition temperature (Tg), of PMMA I and II is shown in Tables 9 and 10 and Figures 13 through 16. The results are accurate to $\pm$ 2°C. As with the changes in molecular weight, the samples irradiated with 253.7 lamps showed a greater decrease in the glass transition temperature than those irradiated with the 300 nm lamps. Also the rate of change of T_g is less in vacuum than in air. Another similarity between T_g and the molecular mass data is that the decrease of T_g with irradiation is faster at the beginning of irradiation than at the end. This similarity between changes in molecular weight (number average) and glass transition can be clearly seen in the linear relationship shown in Figures 17 and 18. These figures also illustrate that the two polymers behave similarly in T_g changes during irradiation.

4.3 Spectral Changes

UV irradiation of PMMA causes an increase in the absorption of the thin film, as shown in Figures 19 and 20. A new band at 285 nm, previously observed by Shultz [4], Frolova [9,10] and Fox et al. [7] was also observed in this work. This band is in the region usually associated with carbonyl

chromphores and is believed to result from carbonyl groups in the polymer chain itself rather than from low molecular mass photolysis products.

The only changes in the IR spectrum of PMMA during the irradiation were a broadening of the carbonyl band at 5.71 μm (1750 cm^{-1}) and the appearance of small new bands at 6.19-6.10 μm (1610-1640 cm^{-1}). The latter bands are attributed to olefinic unsaturation produced during the photolytic chain scission.

As for changes in molecular mass and glass transition temperature changes, the spectral changes are much greater following irradiation with 253.7 nm lamps than with 300 nm lamps.

4.4 Loss of Volatiles from Polymer

The percentage mass loss during the irradiation of PMMA I and II are shown in Tables 11 and 12. At the end of 8 hours of exposure to 253.7 nm lamps, the mass losses were 1.39% and 1.55% in air and under vacuum, respectively. For PMMA I and II irradiated with 300 nm lamps, the mass losses after 64 hours of exposure were 3.68% in air and 4.3 % under vacuum.

From the above data, the mass losses in vacuum are higher than in air. This could be explained by the fact that in vacuum there is more diffusion of the volatile products out of the film than in air. Another observation is that the mass loss of PMMA irradiated with 253.7 nm lamps is much lower than that obtained with 300 nm lamps at equivalent levels of degradation.

5. CONCLUSIONS AND FURTHER STUDIES

The test data show that UV irradiation of PMMA caused a rapid decrease in the molecular mass accompanied by small amount of volatile products. This observation is characteristic of random scission degradation. Molecular mass and T_g data further show that, while the intensity of the 300 nm lamps at 253.7 nm was about one tenth than that of 253.7 nm lamps, the quantum yield was only about one fourth. This suggests that UV wavelengths greater than 253.7 nm play a role in the degradation and that the longer wavelength radiation results in a different degradation mechanism than for 253.7 nm. The mechanism at the longer wavelength may be at least in part a thermal degradation, (unzipping).

Mass losses data show that exposure to 300 nm lamps results in a greater weight loss than exposure to 253.7 lamps. These data provide a further indication that the mechanism of degradation is a combination of thermal and random scission, with thermal degradation being primarily induced at wavelengths greater than 253.7 nm.

Additional research on the degradation of PMMA is needed to study the effect of UV light greater than 253.7 nm in wavelength and visible light (separately or in combination). Specifically, it is proposed that the following exposure studies be done to meet the initial objectives:

1) exposure to 300 nm lamps with filters to remove the 253.7 nm wavelength light

2) exposure to 350 nm lamps

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3) exposure to a combination of UV-visible light (300-700 nm)

4) exposure to 546 nm (green) light and 436 nm (blue) light separately.

Such studies, combined with studies of simulated natural weathering are needed to more fully characterize the mechanisms of degradation under these different conditions. Once the degradation mechanisms are characterized, the feasibility of utilizing accelerated aging (weathering) tests to predict long-term performance of the polymer can be determined.

6. REFERENCES

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Table 1. Molecular Weight Changes, Quantum Yield for PMMA I
Irradiated with 253.7 nm in Air

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} - 1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	189	152	0.0	0.0
0.5	1.285	168	135	0.126	4.53
1.0	2.57	156	127	0.197	3.55
1.5	3.855	142	116	0.310	3.72
2.0	5.14	137	111	0.369	3.32
3.0	7.71	119	98	0.551	3.31
4.0	10.28	107	89	0.708	3.19
5.0	12.85	92	77	0.974	3.51
6.0	15.42	82	68	1.235	3.71
8.0	20.56	58	50	2.040	4.59

Table 2. Molecular Mass Changes and Quantum Yields for PMMA I
During Irradiation with 253.7 nm Lamps in Vacuum

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} -1$	Quantum Yield $\phi_{cs} \times 10^2$
0.0	0.0	189	152	0.0	0.0
0.5	1.285	173	139	0.092	3.31
1.0	2.57	158	127	0.197	3.55
1.5	3.855	151	121	0.256	3.07
2.0	5.14	143	116	0.310	2.79
3.0	7.71	135	103	0.476	2.86
4.0	10.28	113	92	0.652	2.93
5.0	12.85	109	88	0.727	2.62
6.0	15.42	97	78	0.949	2.85
8.0	20.56	90	72	1.111	2.5

Table 3. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 253.7 nm Lamps in Air

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} -1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	248	197	0.0	0.0
0.5	1.285	214	171	0.152	4.31
1.0	2.57	201	157	0.255	3.57
1.5	3.855	176	140	0.407	3.80
2.0	5.14	167	135	0.459	3.21
3.0	7.71	150	120	0.642	3.00
4.0	10.28	126	102	0.931	3.26
5.0	12.85	109	89	1.2	3.40
6.0	15.42	94	77	1.56	3.64
8.0	20.56	67	55	2.58	4.51

Table 4. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 253.7 nm Lamps in Vacuum

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} - 1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	248	197	0.0	0.0
0.5	1.285	219	177	0.113	3.16
1.0	2.57	197	158	0.247	3.46
1.5	3.855	190	151	0.305	2.86
2.0	5.14	173	141	0.397	2.78
3.0	7.71	152	122	0.615	2.87
4.0	10.28	133	108	0.824	2.88
5.0	12.85	126	102	0.931	2.60
6.0	15.42	112	89	1.213	2.83
8.0	20.56	102	82	1.40	2.45

Table 5. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 300 nm Lamps in Air

Exposure Time in Hours	$I_a \cdot T \times 10^{19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}np} -1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	189	152	0.0	0.0
2.0	2.57	178	143	0.063	1.13
4.0	5.14	168	135	0.126	1.13
8.0	10.28	157	124	0.226	1.02
16.0	20.56	138	108	0.407	0.91
24.0	30.84	130	102	.490	0.80
32.0	41.12	118	92	0.652	0.79
48.0	61.68	101	80	0.90	0.68
64.0	82.24	88	69	1.203	0.68

Table 6. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 300 nm Lamps in Vacuum

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}np} - 1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	189	152	0.0	0.0
2.0	2.57	183	144	0.056	1.01
4.0	5.14	178	138	0.101	0.91
8.0	10.28	166	128	0.188	0.94
16.0	20.56	143	117	0.299	0.67
24.0	30.84	130	104	0.462	0.69
32.0	41.12	116	96	0.583	0.66
48.0	61.68	104	84	0.810	0.61
64.0	82.24	90	73	1.082	0.61

Table 7. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 300 nm Lamps in Air

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} - 1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	248	197	0.0	0.0
2.0	2.57	232	183	0.077	1.08
4.0	5.14	216	168	0.173	1.21
8.0	10.28	192	150	0.313	1.10
16.0	20.56	166	131	0.504	0.88
24.0	30.84	151	116	0.698	0.81
32.0	41.12	141	110	0.791	0.69
48.0	61.68	119	94	1.096	0.64
64.0	82.24	101	79	1.494	0.65

Table 8. Molecular Mass Changes and Quantum Yields for PMMA II
During Irradiation with 300 nm Lamps in Vacuum

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\dfrac{\overline{M}_{no}}{\overline{M}_{np}} -1$	Quantum Yield $\phi cs \times 10^2$
0.0	0.0	248	197	0.0	0.0
2.0	2.57	234	185	0.065	0.91
4.0	5.14	216	171	0.152	1.06
8.0	10.28	202	161	0.224	0.78
16.0	20.56	181	145	0.359	0.63
24.0	30.84	162	130	0.515	0.60
32.0	41.12	141	113	0.743	0.65
48.0	61.68	126	102	0.931	0.54
64.0	82.24	112	91	1.165	0.51

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Table 9. Glass Transition Temperatures of PMMA I and II
During Irradiation with 253.7 nm Lamps

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	GLASS TRANSITION TEMPERATURE °C			
		IN AIR		UNDER VACUUM	
		PMMA #1	PMMA #2	PMMA #1	PMMA #2
0.0	0.0	115	116	115	116
0.5	1.285	113	114	113	113
1.0	2.57	110	110	111	111
1.5	3.855	108	108	110	109
2.0	5.14	106	106	108	108
3.0	7.71	104	104	106	106
4.0	10.28	103	103	105	104
5.0	12.85	101	100	102	102
6.0	15.42	99	99	100	101
8.0	20.56	96	96	98	98

Table 10. Glass Transition Temperatures of PMMA I and
II During Irradiation with 300 nm Lamps

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	GLASS TRANSITION TEMPERATURE °C			
		IN AIR		UNDER VACUUM	
		PMMA #1	PMMA #2	PMMA #1	PMMA #2
0.0	0.0	115	116	115	116
2.0	2.57	113	114	114	114
4.0	5.14	111	111	112	112
8.0	10.28	109	110	110	110
16.0	20.56	108	108	109	109
24.0	30.84	107	107	108	109
32.0	41.12	105	106	107	107
48.0	61.68	104	105	105	106
64.0	82.24	103	103	104	105

Table 11. Percent Weight Loss in PMMA I and II During
Irradiation with 253.7 nm Lamps

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	% WEIGHT LOSS			
		IN AIR		UNDER VACUUM	
		PMMA #1	PMMA #2	PMMA #1	PMMA #2
0.0	0.0	0.0	0.0	0.0	0.0
0.5	1.285	0.0	0.0	0.0	0.0
1.0	2.57	0.0	0.0	0.0	0.0
1.5	3.855	0.0	0.0	0.0	0.0
2.0	5.14	0.15	0.21	0.22	0.25
3.0	7.71	0.40	0.40	0.45	0.42
4.0	10.28	0.62	0.61	0.70	0.66
5.0	12.85	0.85	0.90	0.95	0.96
6.0	15.42	1.01	1.09	1.18	1.15
8.0	20.56	1.36	1.42	1.52	1.59

Table 12. Percent Weight Loss in PMMA I and II During
Irradiation with 300 nm Lamps

Exposure Time in Hours	$I_a \cdot T \times 10^{-19}$ Photon/cm^3	% WEIGHT LOSS			
		IN AIR		UNDER VACUUM	
		PMMA #1	PMMA #2	PMMA #1	PMMA #2
0.0	0.0	0.0	0.0	0.0	0.0
2.0	2.57	0.0	0.0	0.0	0.0
4.0	5.14	0.22	0.20	0.25	0.29
8.0	10.28	0.41	0.37	0.52	0.55
16.0	20.56	0.69	0.59	0.78	0.82
24.0	30.84	0.78	0.72	1.22	1.35
32.0	41.12	1.64	1.67	1.97	1.73
48.0	61.68	2.56	2.63	3.11	2.94
64.0	82.24	3.72	3.66	4.24	4.35
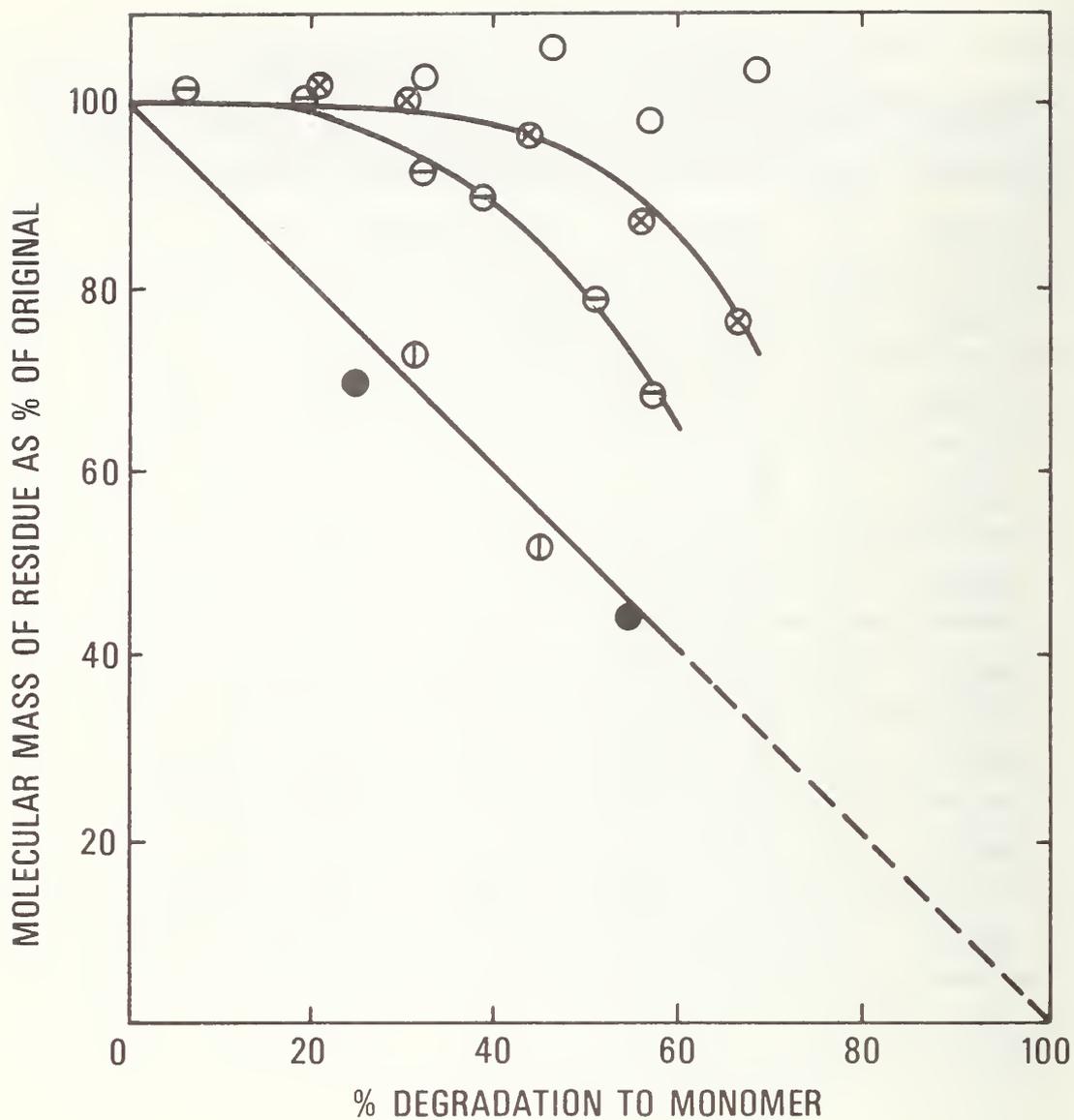
Fig. 1. Grassie [29]. Effect of thermal degradation on the molecular mass of PMMA of various initial molecular mass; ○ 44000, ⊗ 94000, ⊖ 179000, Φ 650000, ● 725000

Fig. 2.   Photochemical reactor.

Fig. 3. Interior view of the photochemical reactor.

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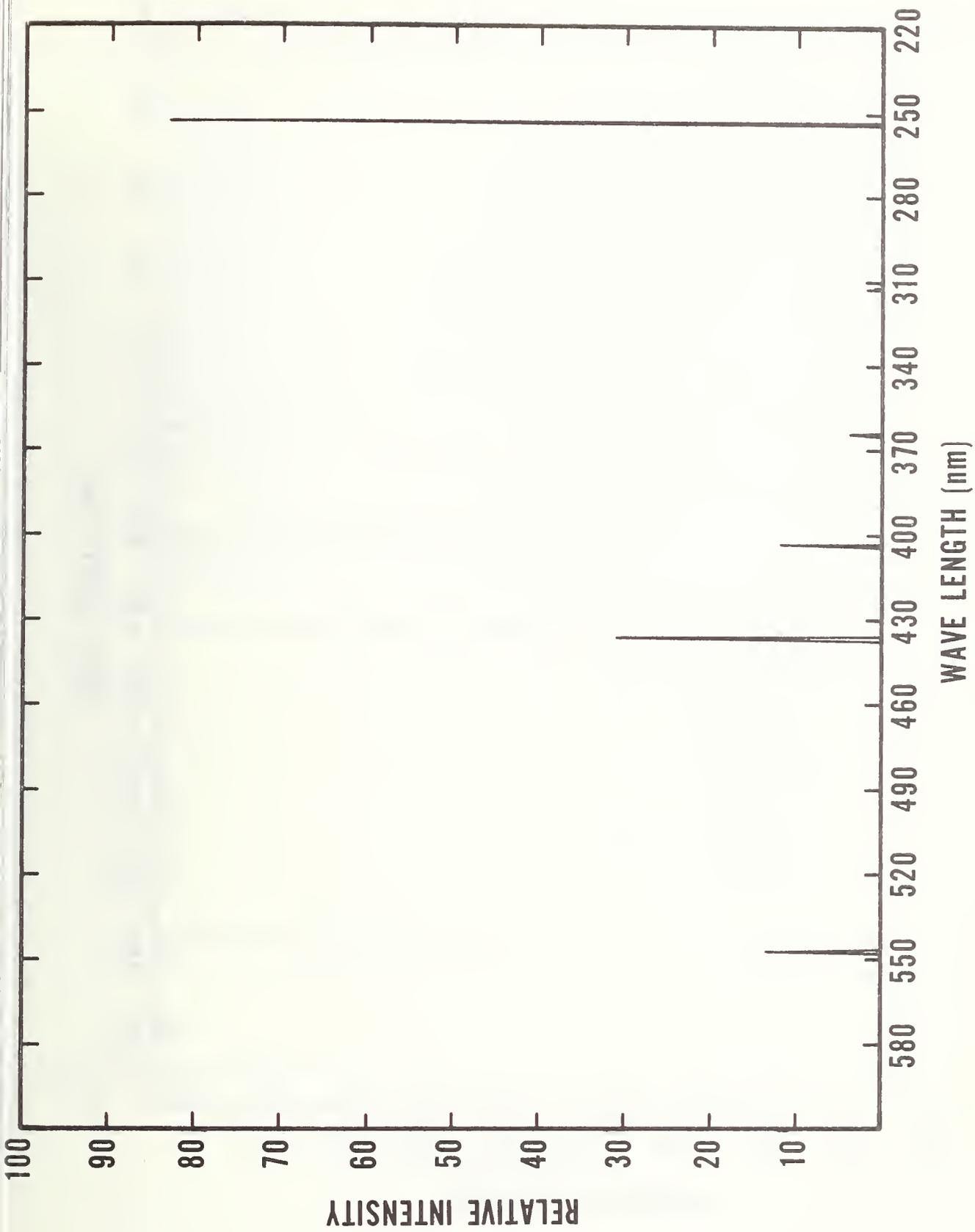
Figure 4. Spectral distribution of 253.7 nm lamp used in the reactor.
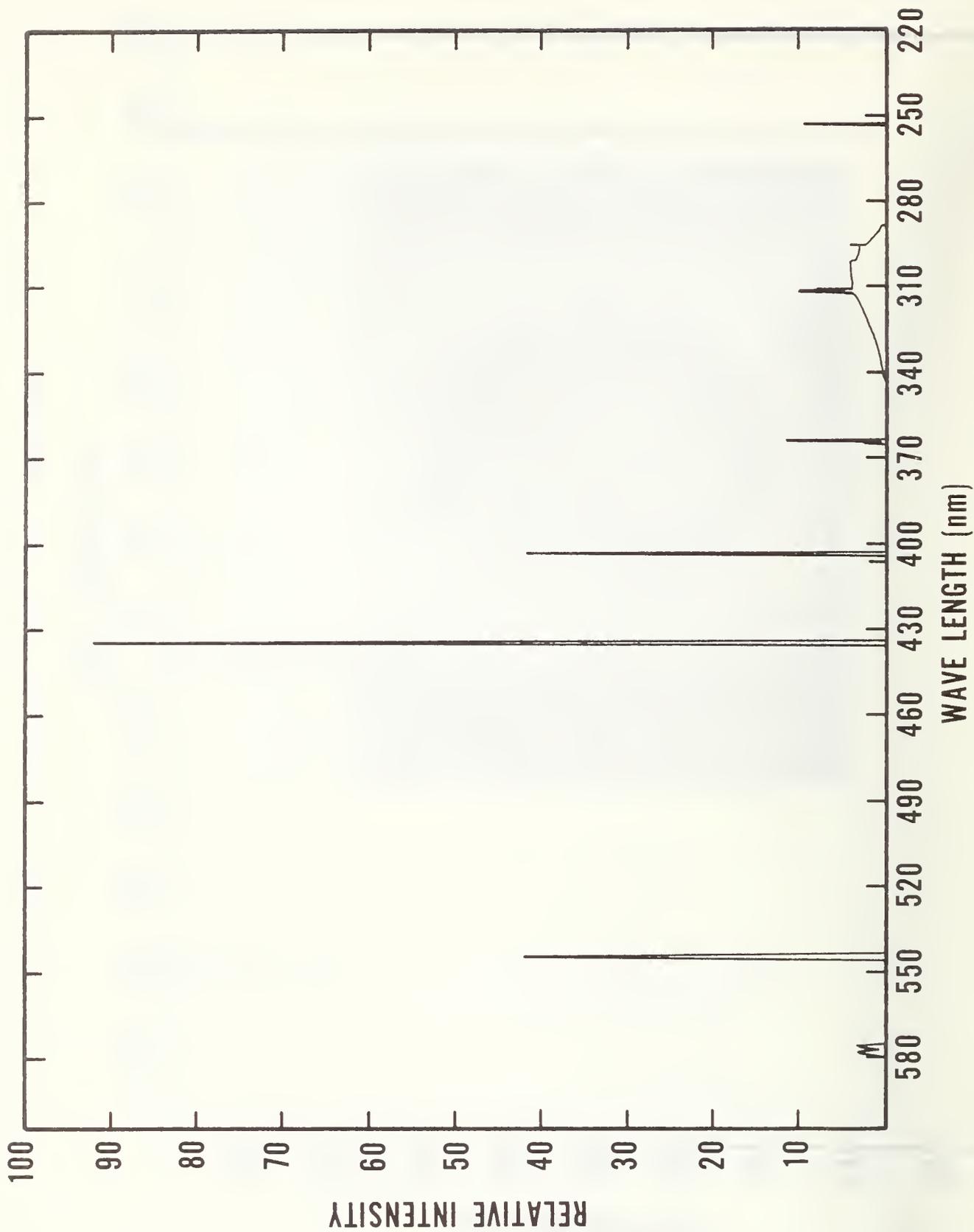
Figure 5. Spectral distribution of 300 nm lamp used in the reactor.

40
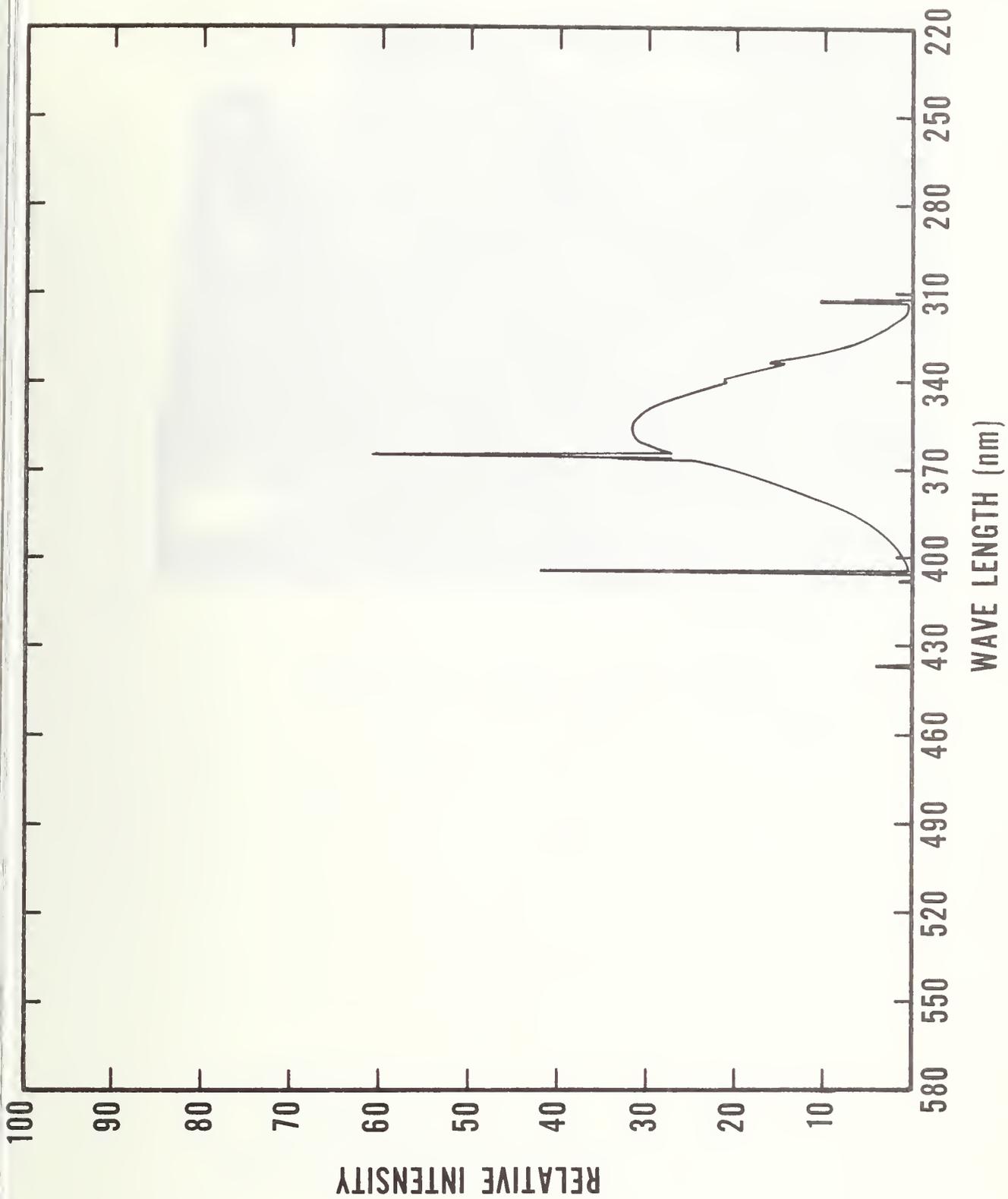
Figure 6. Spectral distribution of 350 nm lamp used in the reactor.

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Fig. 7   Thermomechanical Analyzer (TMA)

  A - sample area and probe

  B - recorder and controls

  H - heater

  L - load
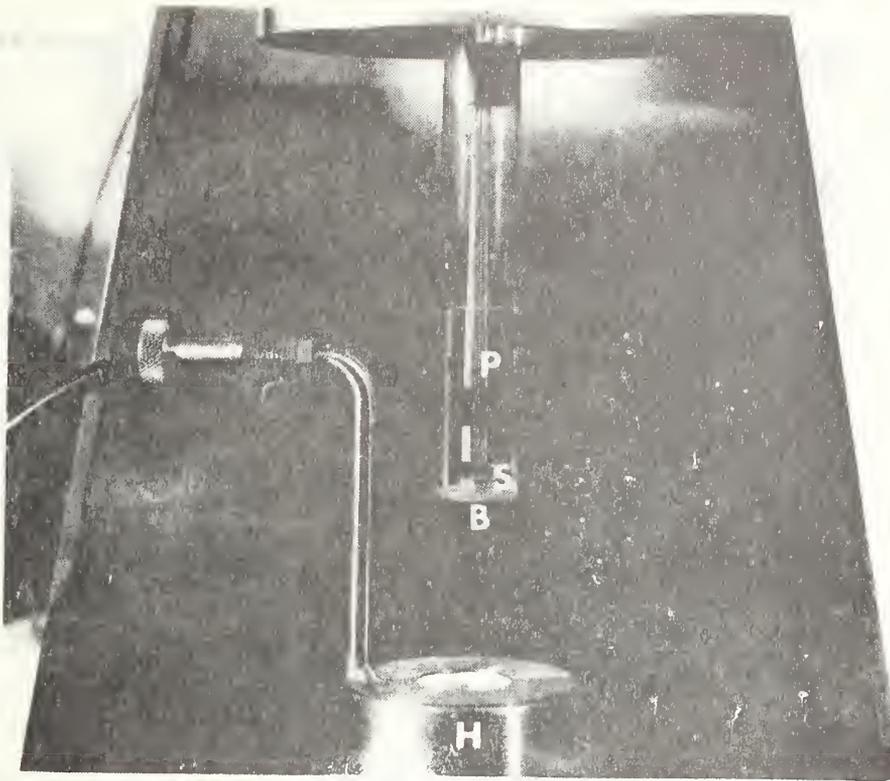
Fig. 8 <u>Thermomechanical Analyzer</u> (Detail)

Close-up view of probe and samples with heater

P - probe

S - sample

B - base

H - heater
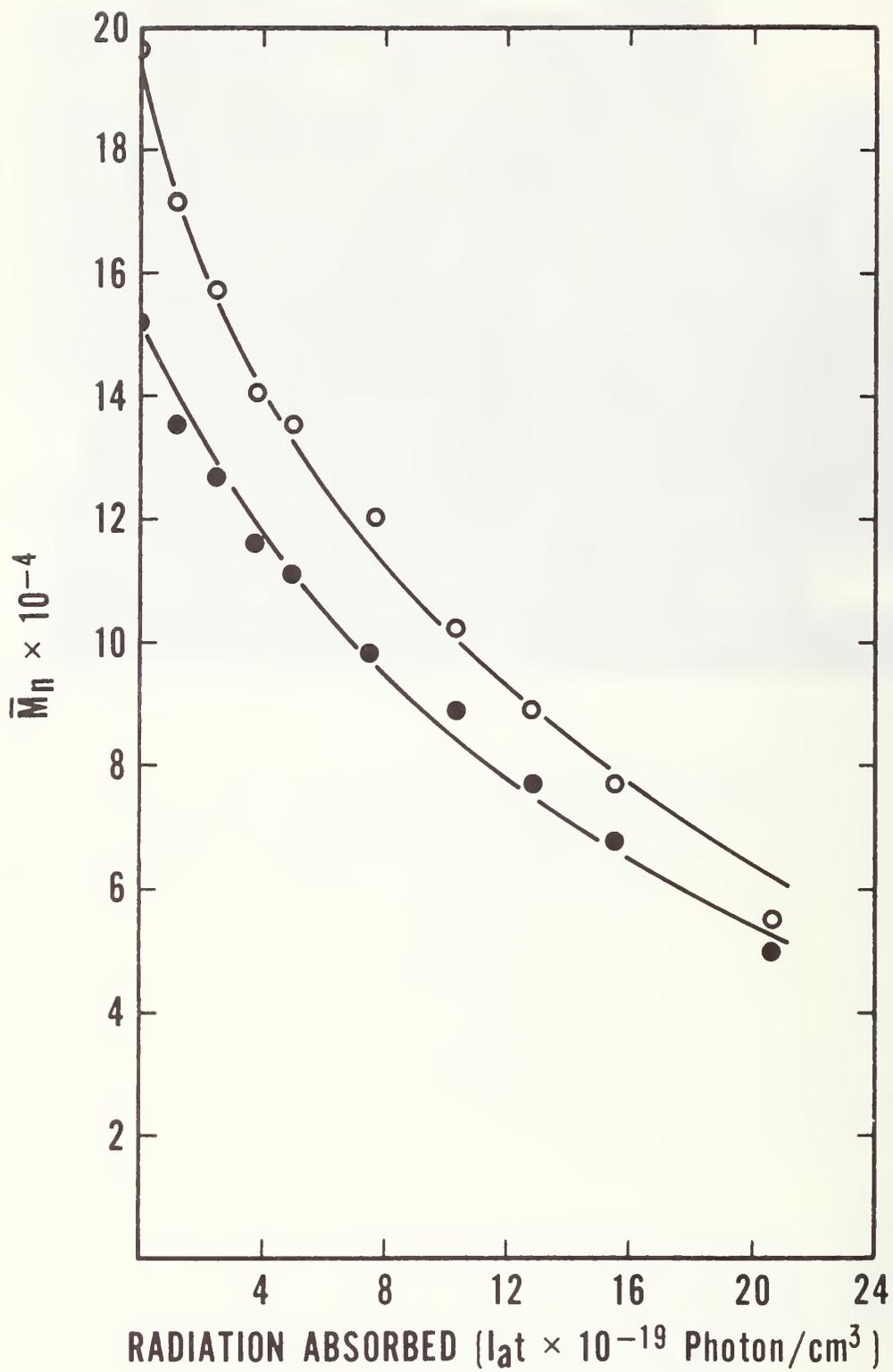
Figure 9. Changes in the number average molecular mass of PMMA during irradiation with 253.7 nm lamps in air; o PMMA I, ● PPMA II.
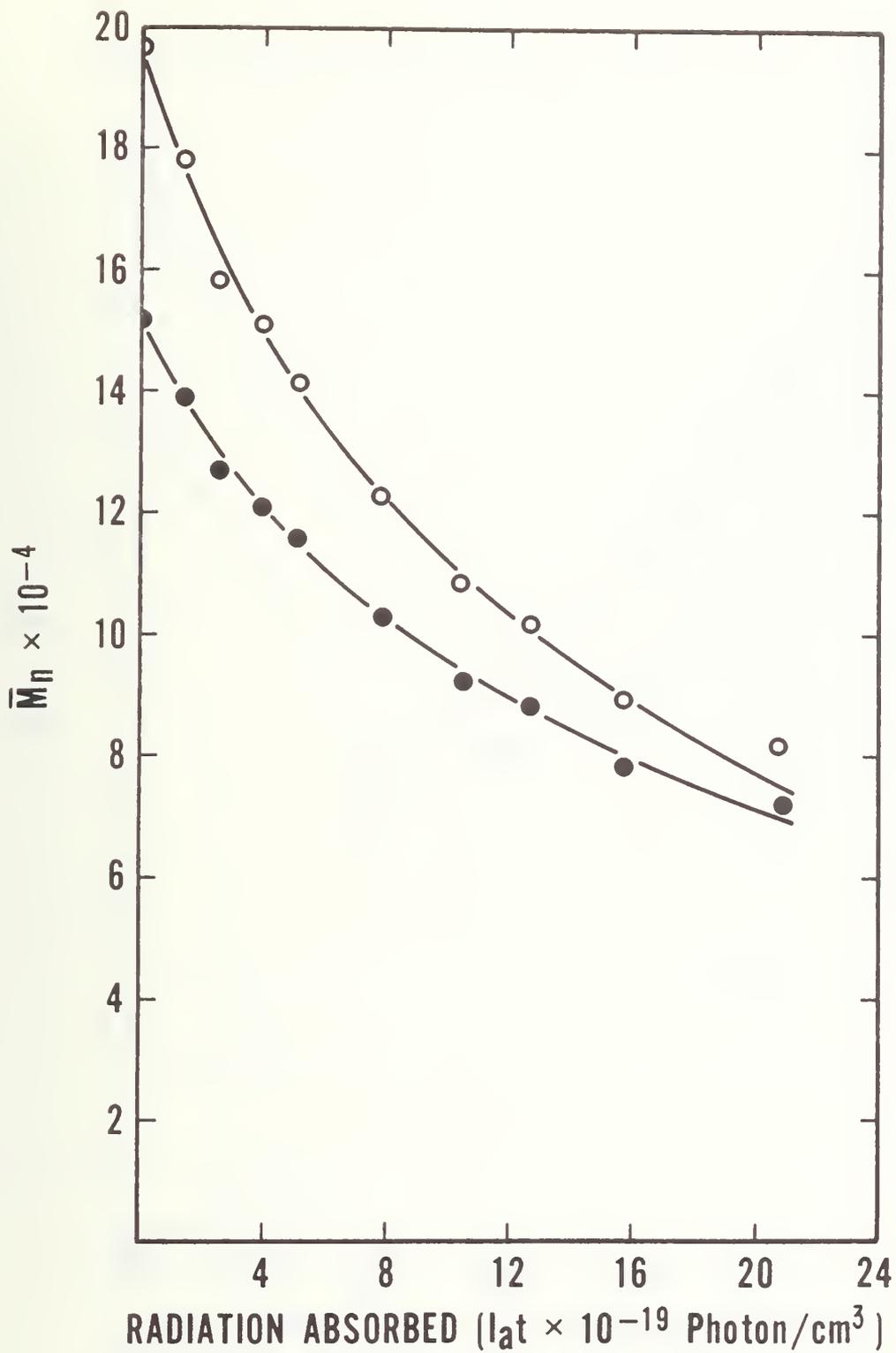
Figure 10. Change in the number average molecular mass of PMMA during irradiation with 253.7 lamps under vacuum; ● PMMA I, o PMMA II.
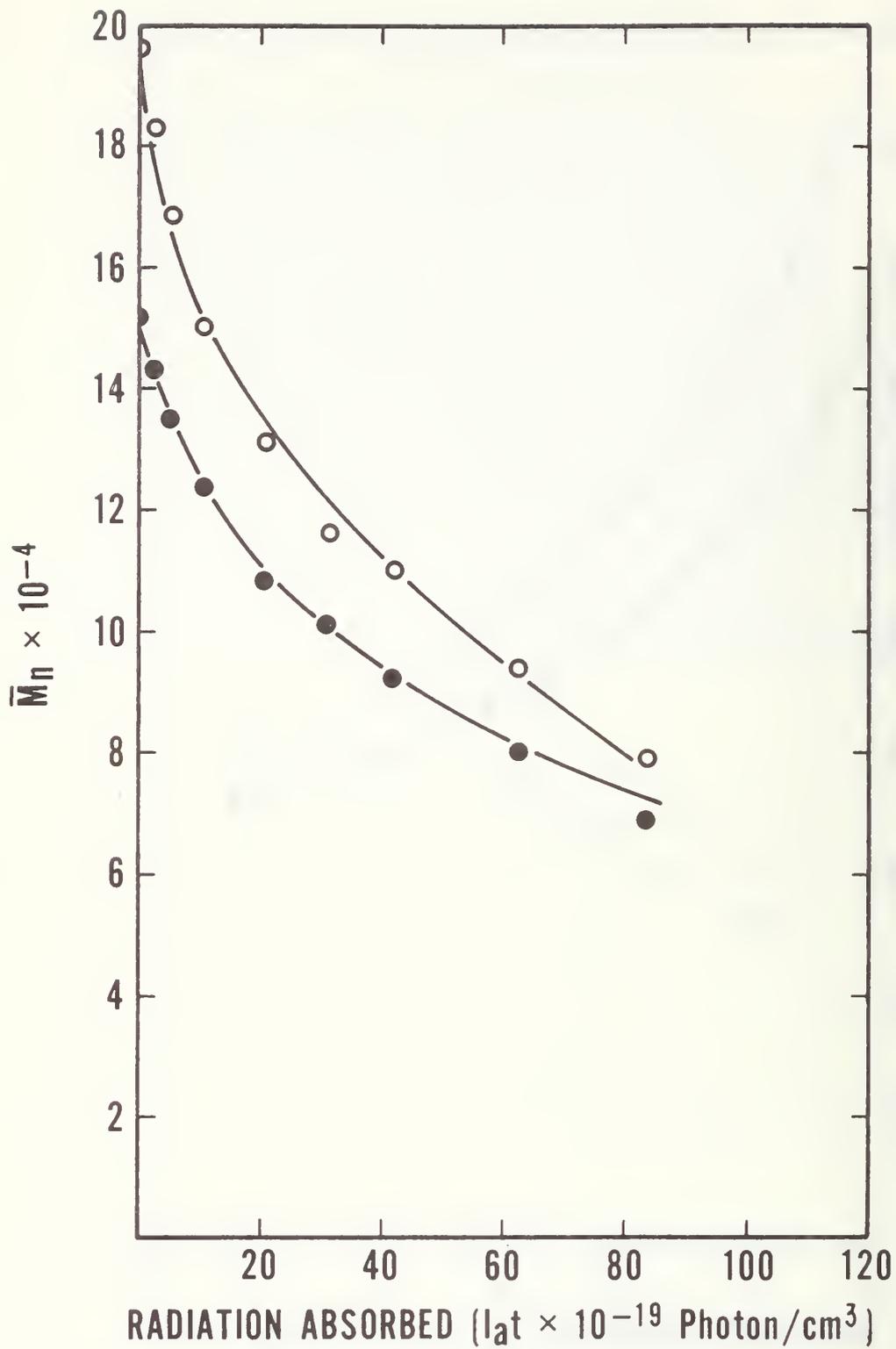
Figure 11. Changes in the number average molecular mass of PMMA during irradiation with 300 nm lamps in air; ● PMMA I, o PMMA II.
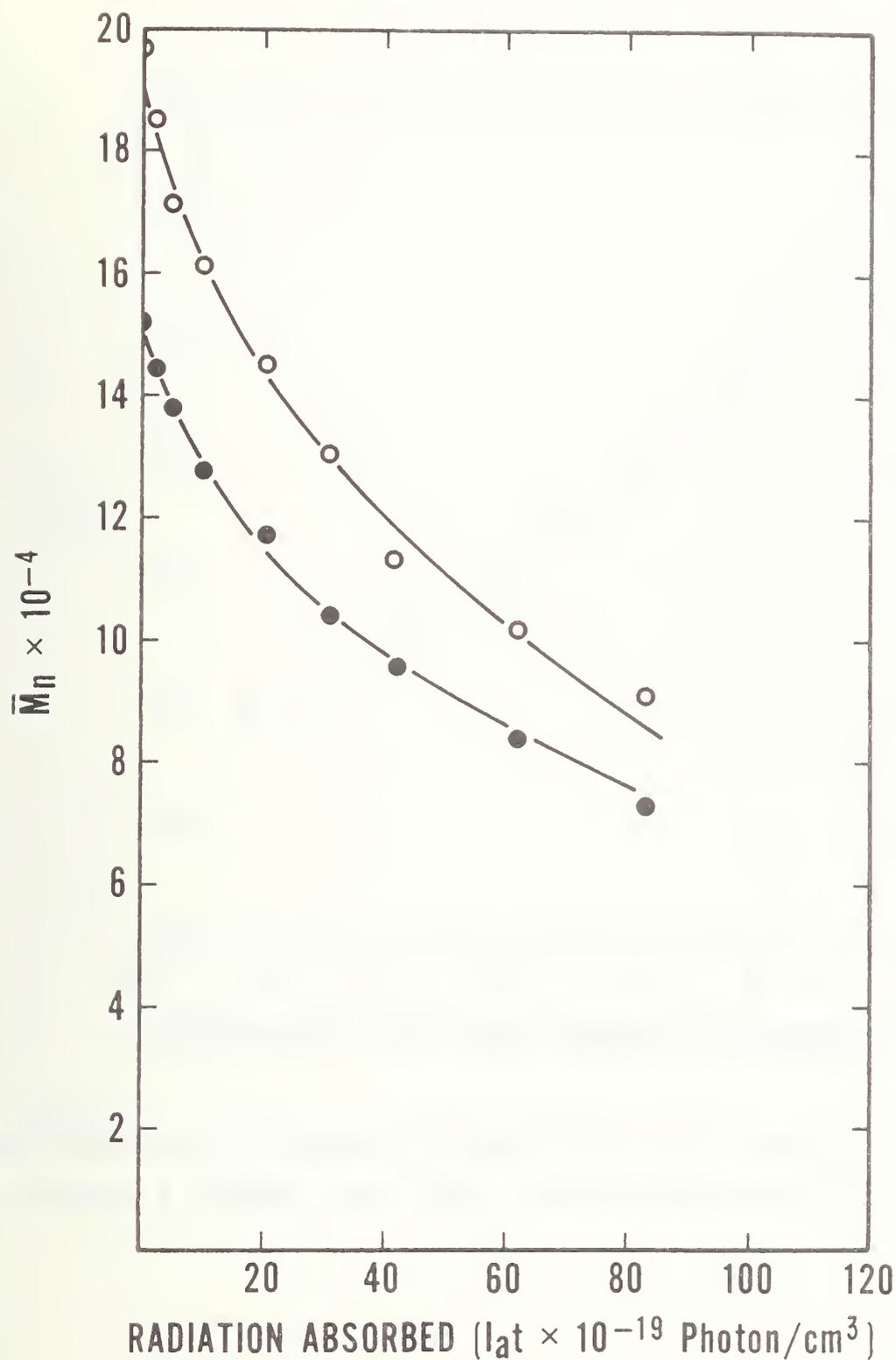
Figure 12. Changes in the number average molecular mass of PMMA during irradiation with 300 nm lamps under vacuum; ● PMMA I, o PMMA II.
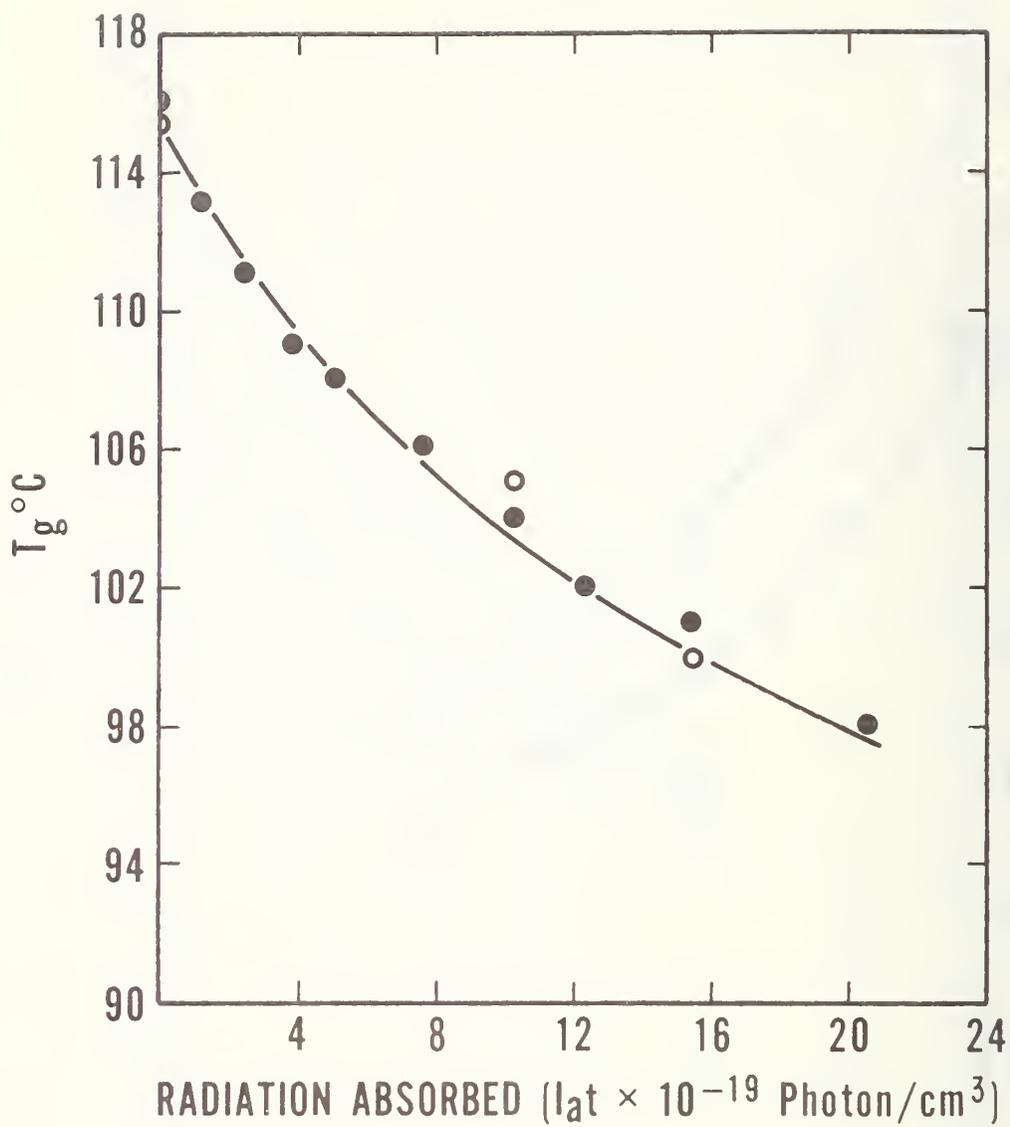
Figure 13. Changes in the glass transition temperature, T_g, of PMMA during irradiation with 253.7 nm lamps in air;o PMMA I, ● PMMA II.
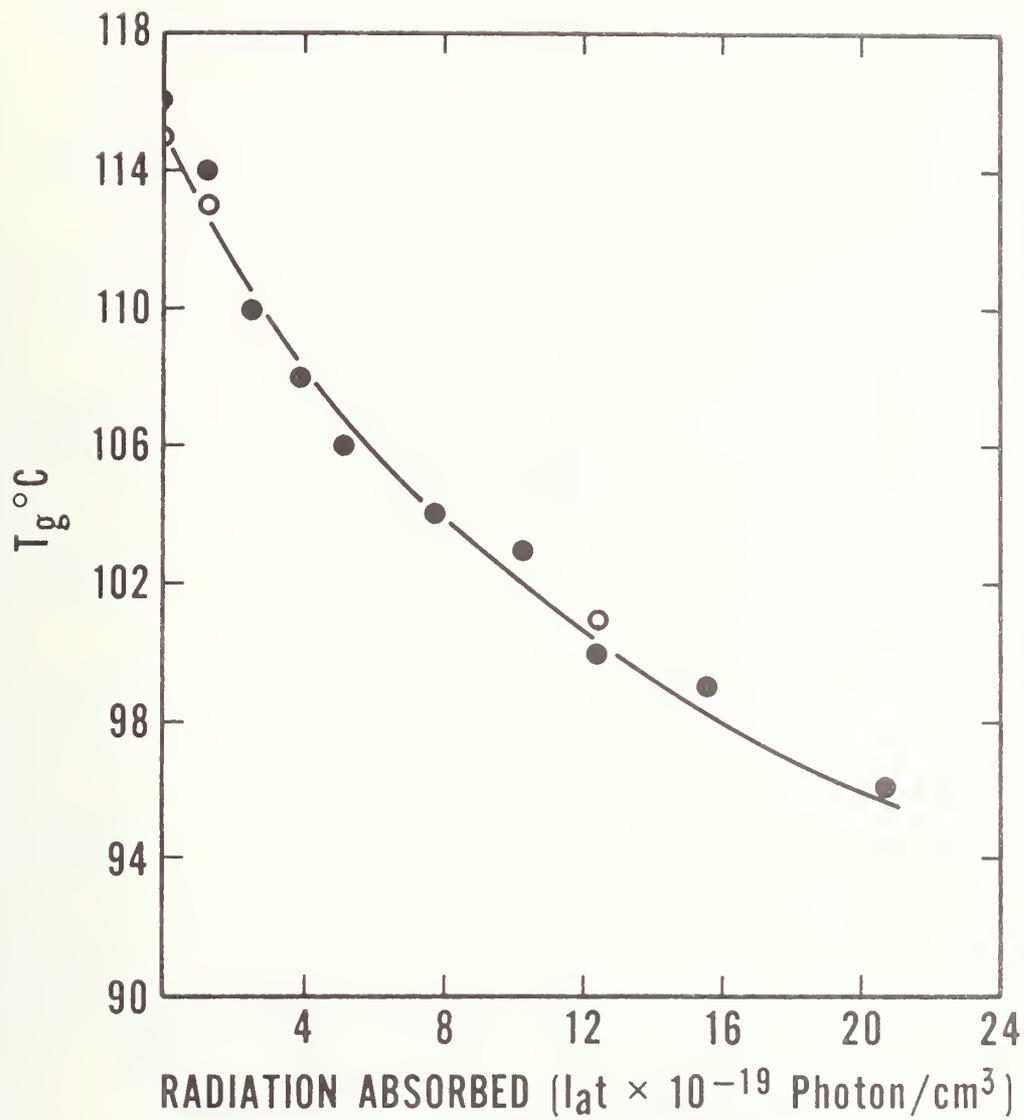
Figure 14.   Changes in the glass transition temperature T_g, of PMMA during irradiation with 253.7 nm under vacuum;o PMMA I, ● PMMA II.
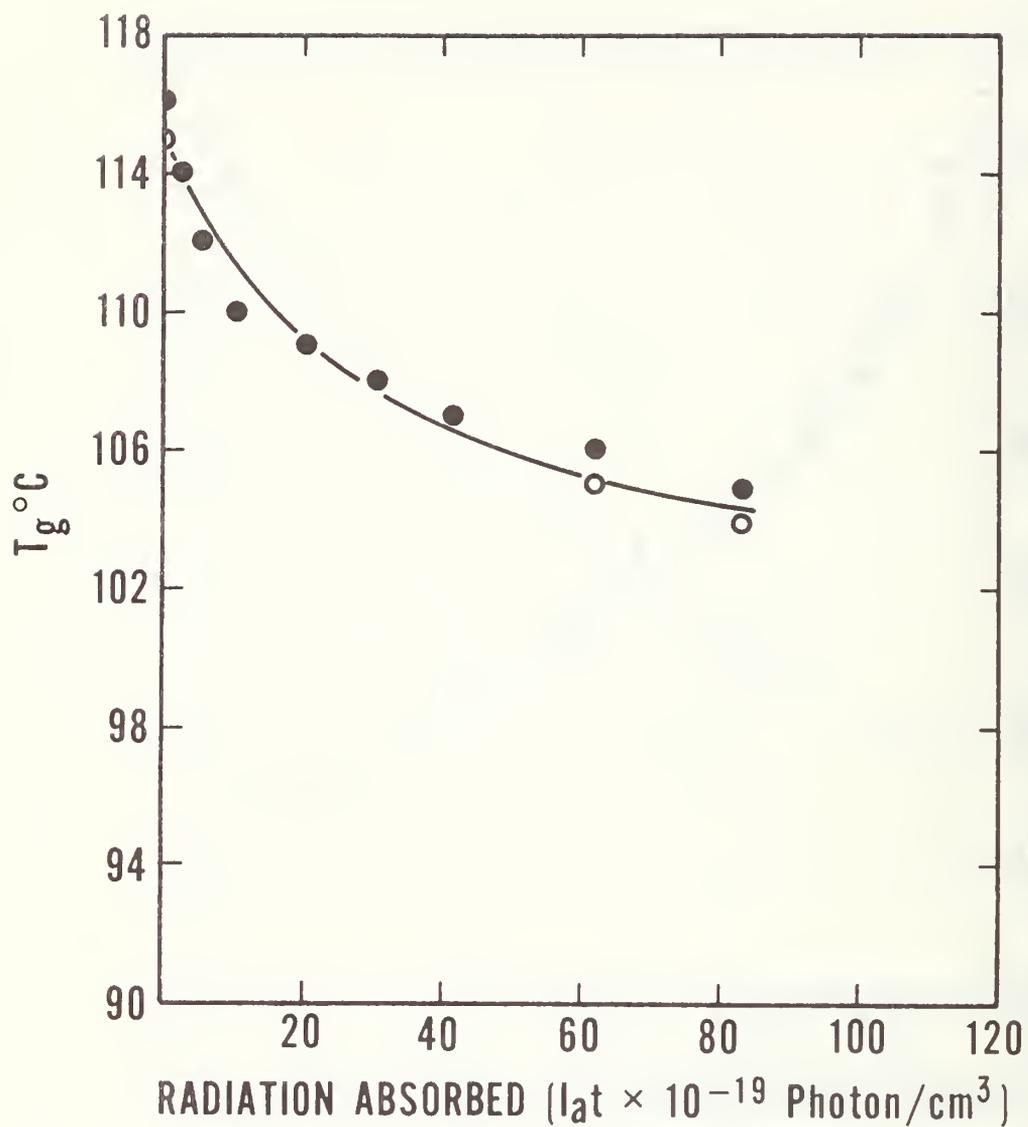
Figure 15. Changes in the glass transition temperature, T_g, of PMMA during irradiation with 300 nm lamps in air; o PMMA I, ● PMMA II.
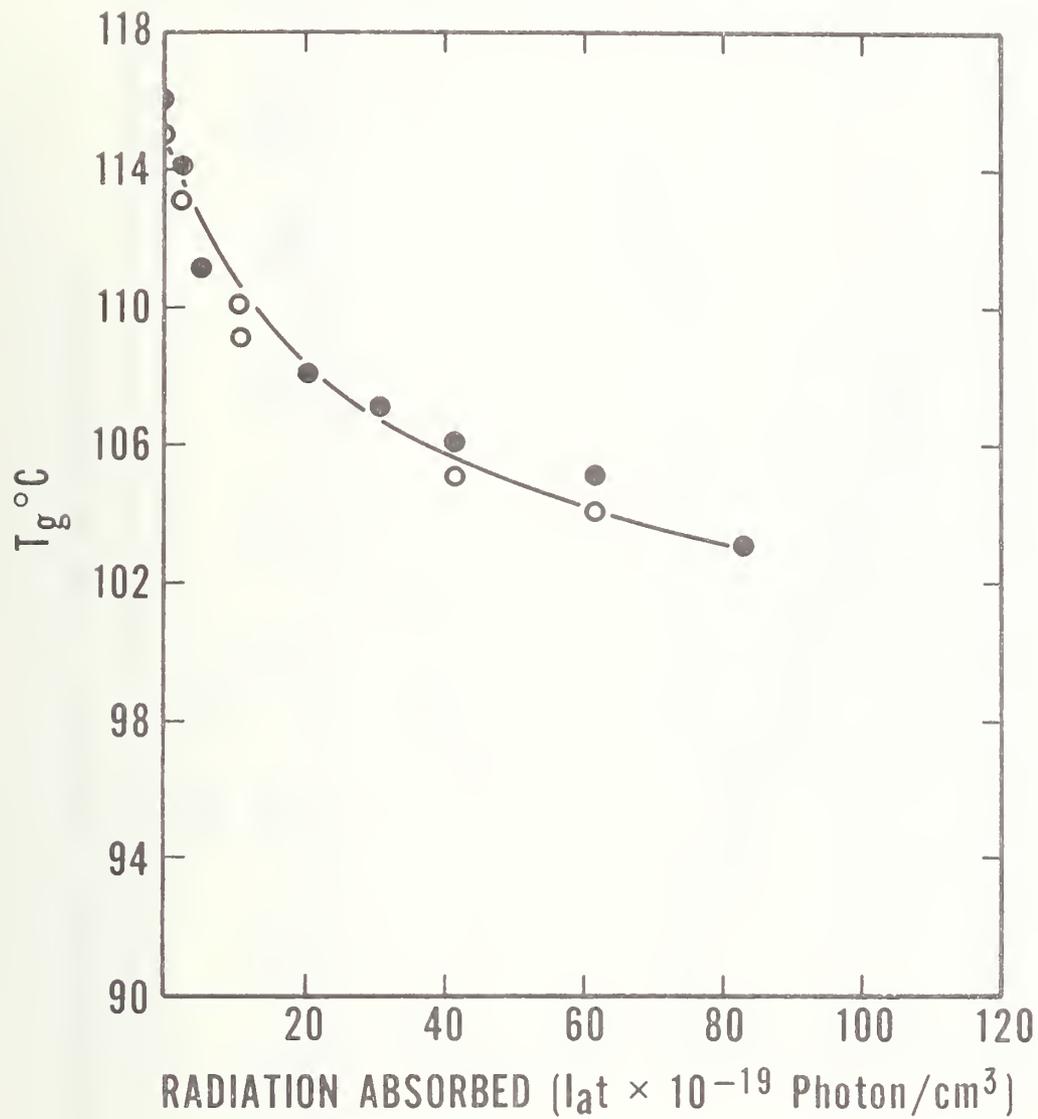
Figure 16. Changes in the glass transition temperature, T_g, of PMMA during irradiation with 300 nm lamps under vacuum; o PMMA I, ● PMMA II.
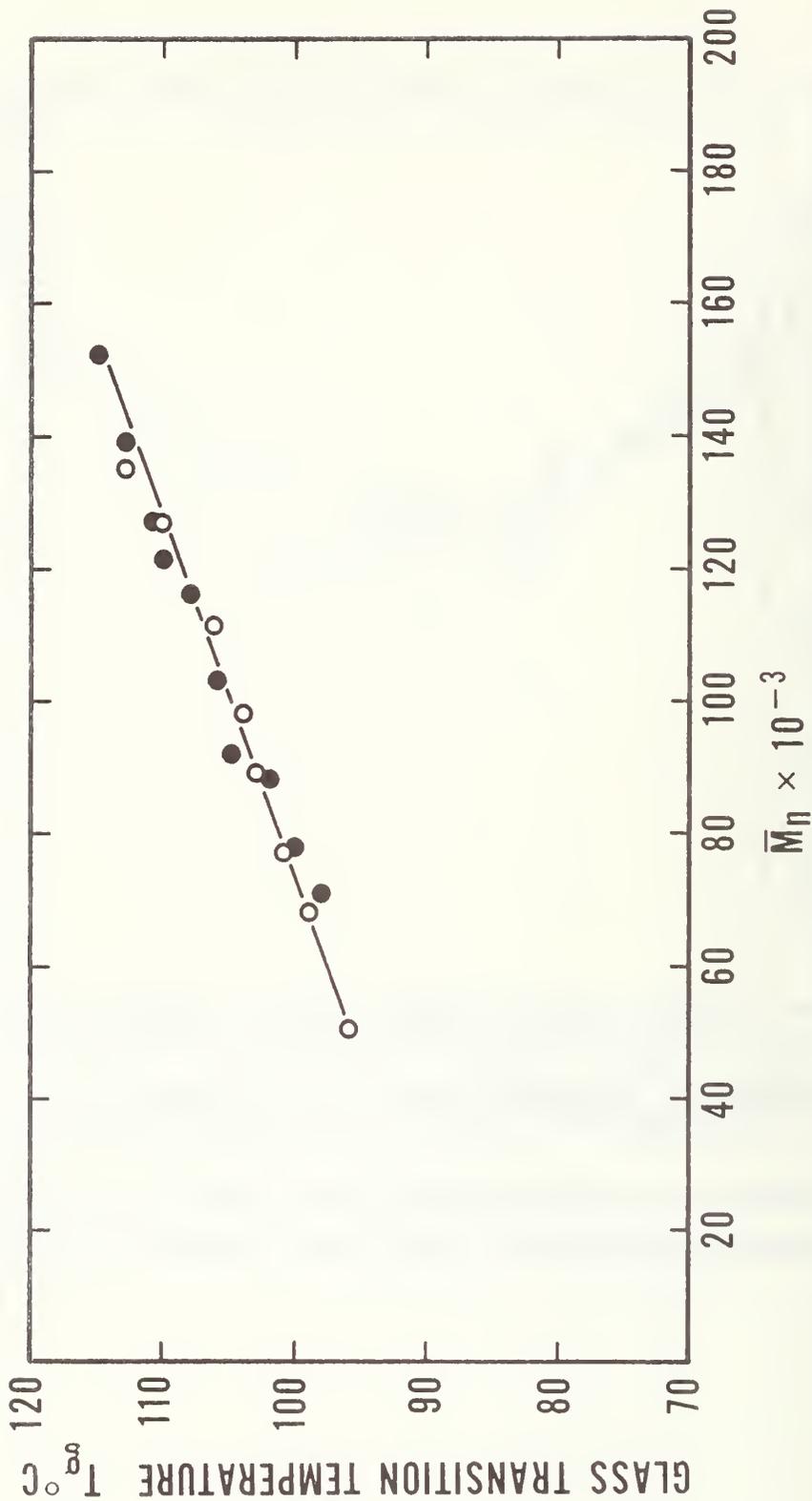
Figure 17. Glass transition temperature vs number average molecular mass for PMMA I irradiated with 253.7 nm lamps; o in air, ● under vacuum.

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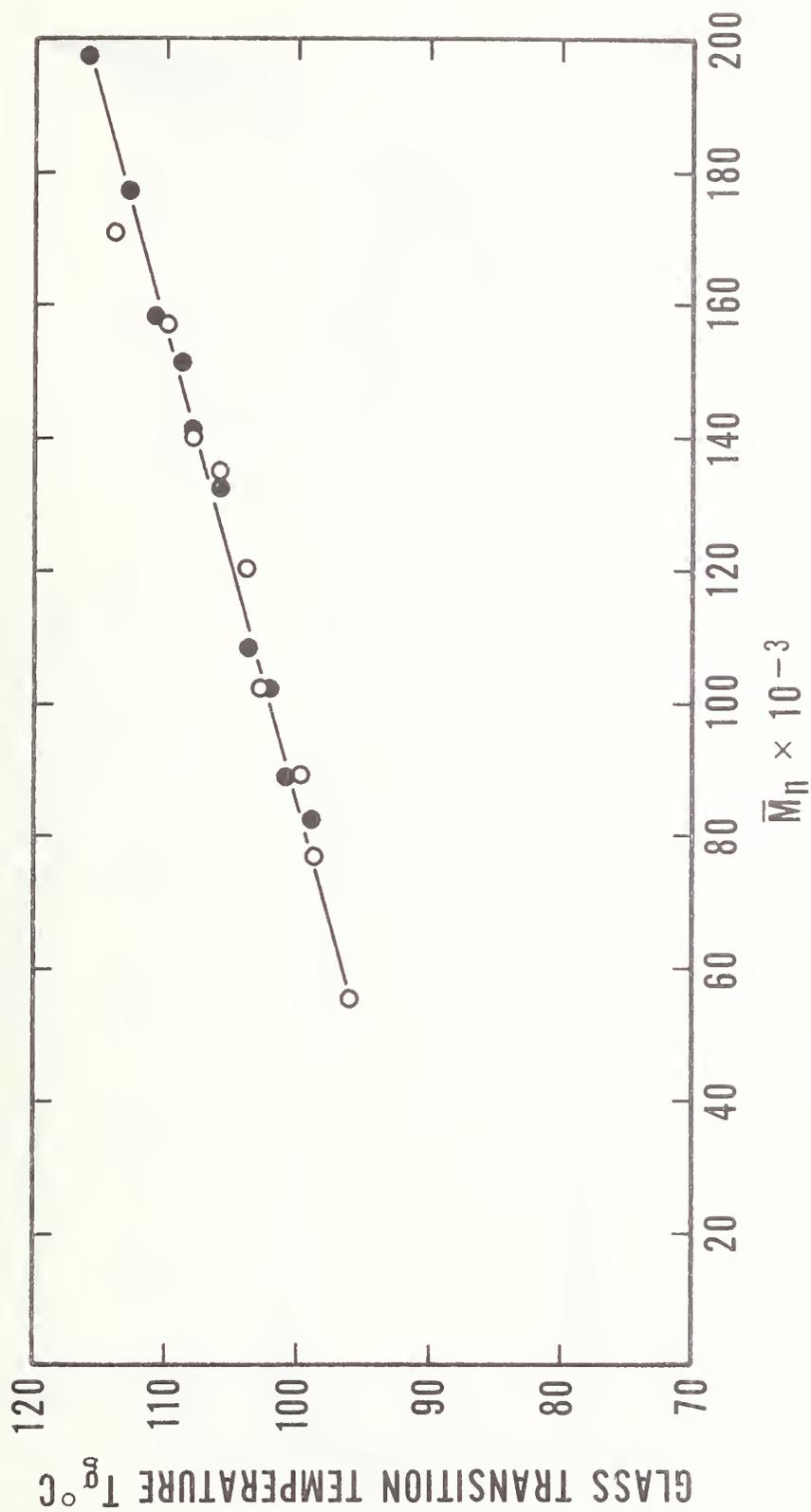
Figure 18. Glass transition temperature vs number average molecular mass for PMMA II during irradiation with 253.7 nm lamps; o in air, ● under vacuum.
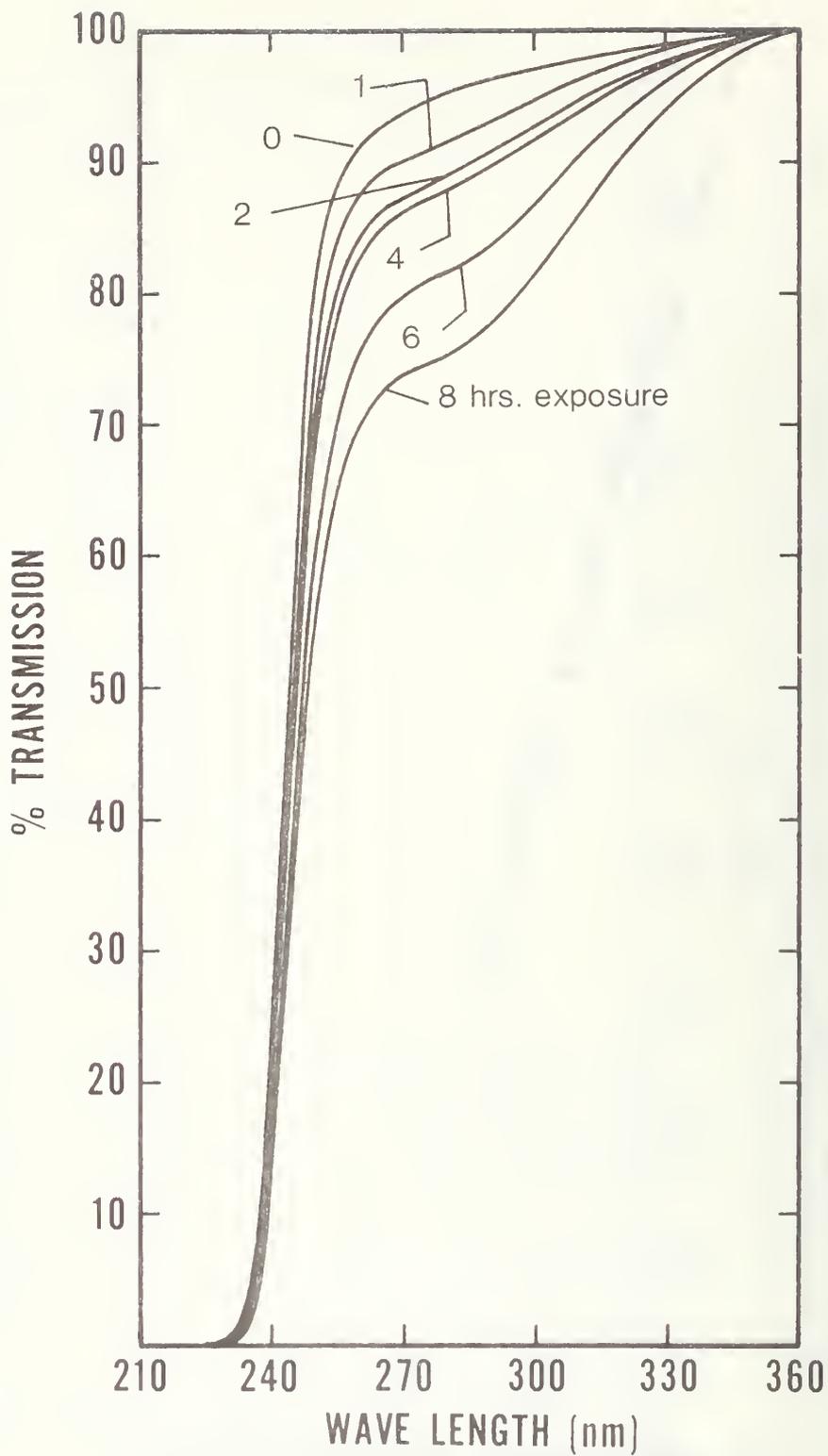
Figure 19. Changes in the ultraviolet spectrum of PMMA II during irradiation with 253.7 nm lamps.
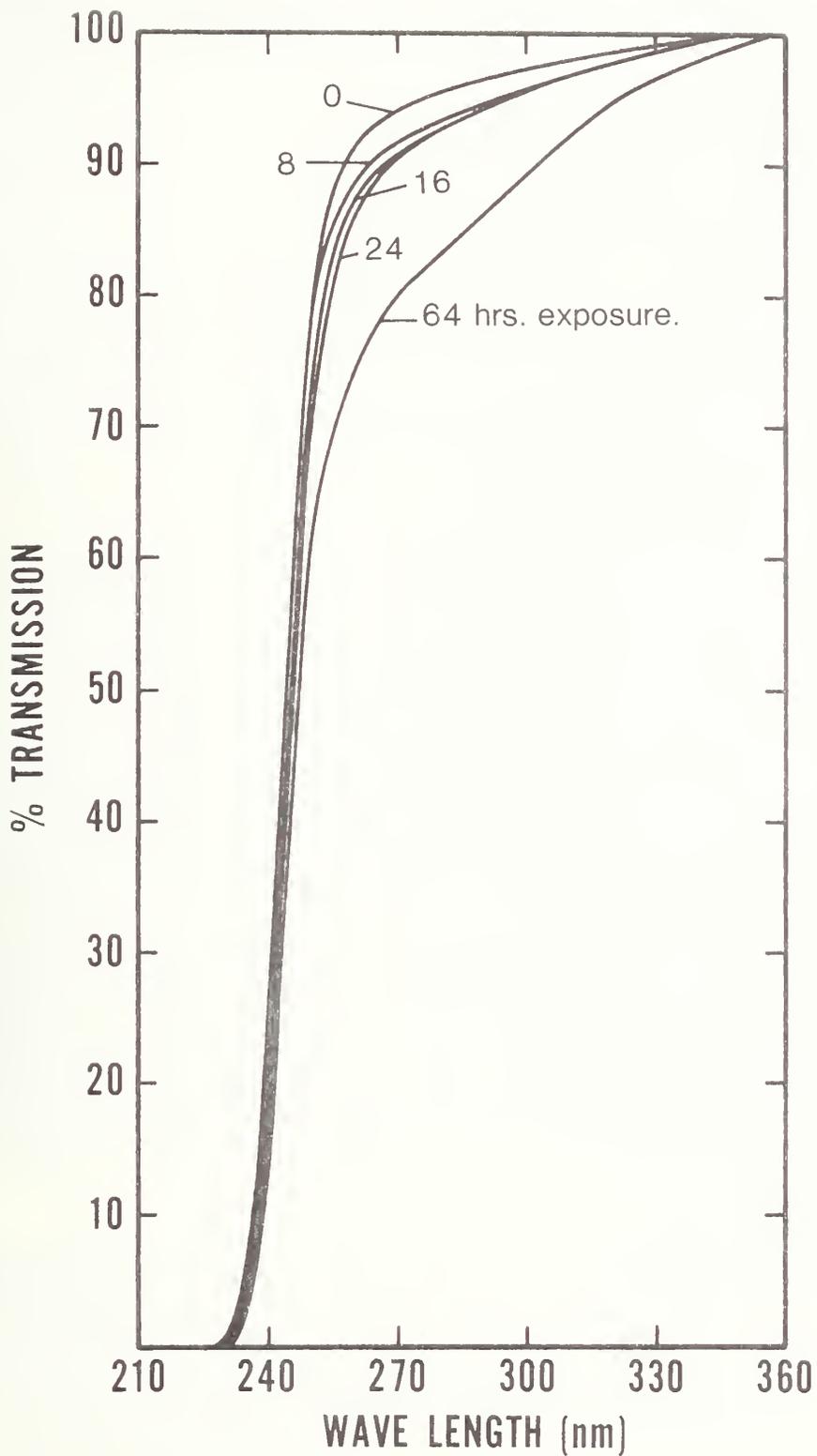
Figure 20. Changes in the ultraviolet spectrum of PMMA II during irradiation with 300 nm lamps.

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This work is done in partial fulfillment of requirements for Doctoral research. The work was performed at the National Bureau of Standards where the author is participating in an IPA Fellowship.

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Although poly(methyl methacrylate), PMMA, is known to degrade when exposed to ultraviolet radiation, studies at wavelengths other than 253.7 nm have not been done. The lack of knowledge about the mechanism of degradation of PMMA at wavelengths other than 253.7 nm hinders efforts to develop short-term test methods for predicting the long-term performance of PMMA in applications in which it is exposed to sunlight. This study was performed to determine the effect of ultraviolet radiation on PMMA and to identify mechanisms of degradation induced by radiation.

Thin films of PMMA of two different molecular weights were irradiated with radiation nominally of 253.7 nm and 300 nm. The irradiations were conducted in air and under vacuum. Exposure at 253.7 nm caused a rapid decrease in molecular mass and loss of a small amount of volatile products, which is a characteristic of random chain scission. The quantum yield was greater in air than in vacuum. Changes in the molecular mass and the glass transition temperature as well as weight loss data indicating that wavelengths bands at greater than 253.7 nm also cause degradation. The data further indicate that the degradation at the longer wavelengths may not be completely random scission.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)
Degradation; photodegradation; poly(methyl methacrylate); UV.

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