

Molar Absorptivity of Poly(methyl Methacrylate) in the Near-Ultraviolet Region

MAUREEN WARNOCK and DONALD G. GARDNER, *Chemistry Department, Illinois Institute of Technology, Chicago, Illinois 60616 and Lawrence Radiation Laboratory, University of California, Livermore, California 94550*

Synopsis

The molar absorptivities of methyl methacrylate monomer and of thermally polymerized, monomer-free poly(methyl methacrylate) have been measured in the range 2200–3000 Å, and smoothed values are presented at wavelength intervals of 20 Å over much of this range. Typical amounts of monomer present in a thermally polymerized bulk polymer and in films cast from CH₂Cl₂ solutions of the bulk polymer have been ascertained. The use of such absorptivity values to determine the amount of monomer present in polymer samples is evaluated.

INTRODUCTION

During the course of an investigation of energy transfer in the system poly(methyl methacrylate), or PMMA, plus small amounts of various additives it became necessary to know as accurately as possible the molar absorptivities of the polymer in the ultraviolet wavelength region. A search of the literature revealed that, although a number of absorbancy studies of PMMA had been made in the ultraviolet region,¹⁻¹³ none provided simultaneously both the completeness of wavelength range and the desired experimental details that would enable one to calculate accurately the absorptivities for the polymer thermally polymerized at 90°C.

Goodeve² made a study of the absorption spectra of methyl methacrylate monomer, the thermally polymerized polymer, and of mixtures of the two at different stages of the polymerization process. The polymer was studied in the form of thin films and polished discs. The data obtained for the solid materials, however, were believed to represent the absorption of various mixtures of the polymer and of residual monomer. Cowley and Melville⁴ determined the ultraviolet absorption spectrum of PMMA by measuring the transmission of a series of films of different thicknesses, as a function of wavelength. The polymer was precipitated twice before being cast as films to ensure that all monomer and solvent traces were removed. The PMMA that they studied, however, had been polymerized with benzoyl peroxide used as an initiator and had a relatively low molecular

weight of about 1×10^5 . Shultz⁷ measured the absorption of lauroyl peroxide-catalyzed PMMA at 2537 Å, using films of the polymer, and obtained an absorptivity of 0.66. This value agreed fairly well with the 0.72 absorptivity he had obtained at 2537 Å for a thermally initiated PMMA sample that had been reprecipitated and washed, to remove monomer.

In Table I the results from the previous investigations of the polymer are presented. Where a continuous spectrum was published, this fact is noted in the table, and absorptivities read from such a curve are listed at a few wavelengths of particular interest in the current investigation.

In the present study it was hoped to obtain the molar absorptivities of PMMA known to be monomer-free and to obtain the apparent absorptivi-

TABLE I
Molar Absorptivities for Poly(methyl Methacrylate)

λ , Å	Goodeve ^a	Cowley and Melville ^b	Shultz ^c	Present work ^d	
				Bulk thermal (90°C) ^e	Monomer- free
2200				248 ± 11	163 ± 8
25				198	136
50				154 ± 6	119 ± 4
75				117	101
2300	87.1			88 ± 6	81 ± 8
25				66	63
50				48 ± 4	46 ± 1
75				34	31
2400	18.6			21.6 ± 0.4	19 ± 3
25					15.5
50	7.9	4.36		9.2 ± 0.2	6.4 ± 0.9
75					4.2
2500				4.0	1.8
25					0.7
37	1.2	1.32	0.72	2.6 ± 0.2	0.37 ± 0.06
50					0.48
75					0.16
2600	0.56	1.15		1.53 ± 0.05	0.09 ± 0.04
50				1.0	
2700	0.24	0.97		0.70	0.07 ± 0.03
50				0.58	
2800	0.14	0.83		0.37 ± 0.04	0.06 ± 0.04
50				0.28	
2900				0.20	
50				0.18	
3000	0.07	0.33		0.16 ± 0.03	0.01 ± 0.05

^a As read from a continuous curve of the absorptivity of the polymer.³

^b Polymerization initiated by benzoyl peroxide.⁴

^c Ref. 7.

^d Error limits are discussed in the text.

^e Determined in *p*-dioxane and in solution of 10% methylene chloride and 90% acetonitrile in the range 2200–2375 Å and in methylene chloride solution in the range 2400–3000 Å.

ties of systems containing residual monomer. The latter systems were the bulk PMMA, thermally polymerized at 70 and 90°C, and thin films made by a single casting of the bulk PMMA from methylene chloride solution. In this work the molar absorptivity $a(\lambda)$ will be used; it is defined as follows:¹⁴ the absorbance $A(\lambda)$ divided by the product of the concentration c (in moles per liter) and the cell length b (in centimeters):

$$a(\lambda) = A(\lambda)/bc \quad (1)$$

The absorbance $A(\lambda)$ is defined as $\log_{10} I_0/I_t$, where I_0 and I_t are the incident and transmitted light intensities, respectively. The apparent absorptivity of the polymer (*vide infra*) is extremely sensitive to small amounts of monomer present in the system, and it has been observed that the concentration of monomer is strongly dependent upon the conditions of polymerization and the subsequent treatment of the polymer.

EXPERIMENTAL

The bulk PMMA was studied in methylene chloride, *p*-dioxane, and solutions of 10% methylene chloride and 90% acetonitrile, and as thin films cast from methylene chloride solution. The monomer-free PMMA was obtained by reprecipitating twice into methanol from CH_2Cl_2 solution and then casting into films. The ultraviolet spectrum of the monomer was obtained in *n*-heptane solution.

The methyl methacrylate monomer used was obtained from the Borden Chemical Company and E. I. du Pont de Nemours and Company. Fisher Spectranalyzed *n*-heptane and methylene chloride; Matheson, Coleman and Bell Spectroquality *p*-dioxane and acetonitrile were used as solvents. The spectra were obtained with a Cary Model 14 recording spectrophotometer. Matched Beckman silica cells were used in the solution work.

The bulk PMMA studied was polymerized at 90°C in a constant-temperature oil bath from methyl methacrylate that had been vacuum-distilled to remove the hydroquinone inhibitor and then stored at -5°C until used. The dissolved gases were removed from the monomer by alternate freezing and thawing under vacuum. The molecular weight of samples of the bulk polymer averaged 9×10^6 . Small pieces of the bulk solid were sanded and rinsed with methylene chloride before being dissolved in the solvent proper.

The monomer-free PMMA was made by dissolving a sanded sample of the polymer in methylene chloride and precipitating the PMMA into methanol. Two such precipitations were carried out. The sample was then put into solution, and a series of films of varied thicknesses was cast.

Films were cast onto a smooth, level, glass surface within circular glass forms; different aliquots of the methylene chloride solution were used to obtain various film thicknesses. When the films were dry, they were lifted from the glass with running water and were mounted in 5×5 cm aluminum frames. These mounted films were stored under vacuum for varied lengths of time, in some cases at temperatures near 80°C. Neutron activation analysis for the Cl content in similar films showed that less than 0.06% by

weight of the solvent remained in the films. The ultraviolet absorption spectra of the PMMA films were then obtained. The surface density of each film was determined by weighing a known area of the film. The film was checked for uniformity by comparing the absorbance at each of the film's four corners at a particular wavelength, usually 2537 Å. The corner giving an average absorbance was used to obtain the ultraviolet spectrum.

Two sets of monomer-free PMMA films were prepared with an 8-month interval between. The absorptivities from each set were in excellent agreement.

The methyl methacrylate monomer, stored at -5°C , was tested for the presence of polymer before its ultraviolet spectrum was determined in *n*-heptane solution.

RESULTS

In Table I are listed values at a few wavelengths of interest for the absorptivities of the bulk, thermal polymer and of the monomer-free PMMA. In Table II are listed the presently determined absorptivities of the methyl methacrylate monomer at various wavelengths, along with previously determined values. Standard deviation error limits are given for a number

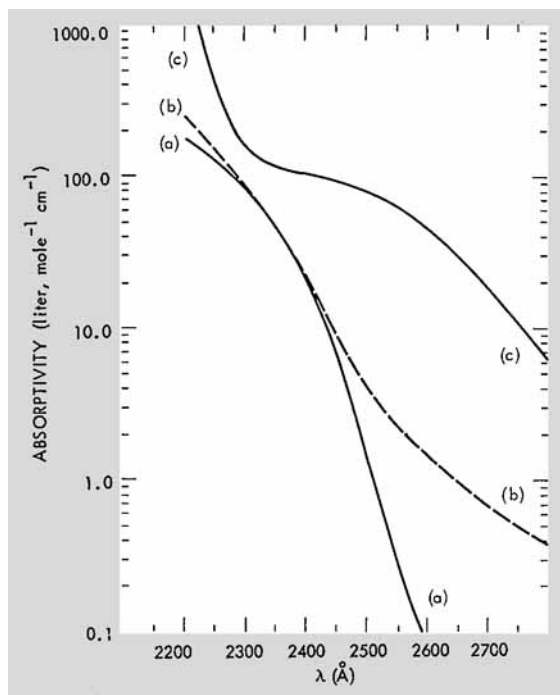


Fig. 1. Absorptivity versus wavelength: (a) monomer-free PMMA polymer; (b) bulk PMMA polymerized at 90°C ; (c) MMA monomer.

TABLE II
 Molar Absorptivities for Methyl Methacrylate Monomer

λ , Å	Goodeve ^a	Melville ^b	Kinell ^c	Present work ^d
2200				1869 ± 62
25				1007 ± 21
50				490 ± 31
75				247 ± 10
2300	251	275		146 ± 15
25				117 ± 13
50				109 ± 12
75				107 ± 14
2400	145	202		102 ± 3
25				97.9
50	126	156		92.4 ± 0.05
75				86.2
2500			97.5	78.0
25				69.5
37	75.9	73	77.6	65.8 ± 0.6
50				61.3
75				51.9
2600	46.8	40	45.9	44.2 ± 0.6
25				36.5
50				30.1
75				21.7
2700	18.6	20	14.2	18.1 ± 0.1
50				10.7
2800	4.4	8	2.9	5.6 ± 0.2
50				3.6
2900				1.6
50				1.3
3000	0.2			0.9 ± 0.1

^a As read from a continuous curve of absorptivity for monomer in hexane solution.²

^b As read from a continuous curve of absorptivity for monomer in hexane solution.¹

^c As read from a continuous curve of absorptivity for monomer in chloroform solution.⁶

^d Monomer in heptane solution; error limits show typical standard deviations from average of seven sets of measurements in the range 2200–2400 Å and from average of four sets of measurements over the remaining range.

of the values. Figure 1 presents the absorptivity as a function of wavelength for the two polymer types, along with that for the monomer.

The bulk polymer absorptivities in the range 2400–3000 Å represent averages over four separate aliquots of a methylene chloride solution of the PMMA, each aliquot being scanned twice. In the range 2200–2375 Å the polymer absorptivities were obtained from five aliquots of a *p*-dioxane solution and from two aliquots of a methylene chloride-acetonitrile solution. The concentration of the bulk solutions was determined in all but one case by the weight difference method, by which a correction was made in the weights for the 2.4% by weight of the monomer that was lost during the evaporation process. In the other case a polymer solution was made up to

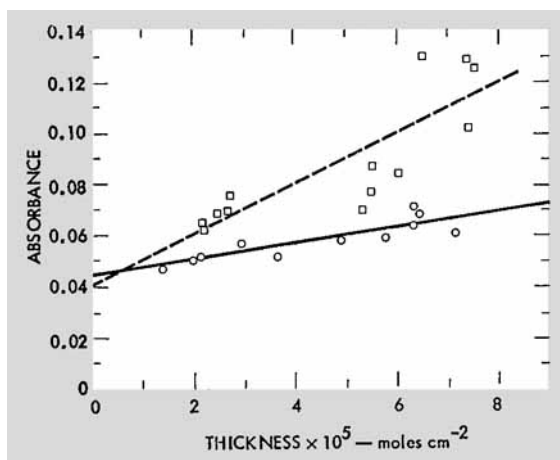


Fig. 2. Absorbance versus thickness of PMMA films at 2537 Å: (□) bulk films containing about 1% monomer; (○) monomer-free PMMA films.

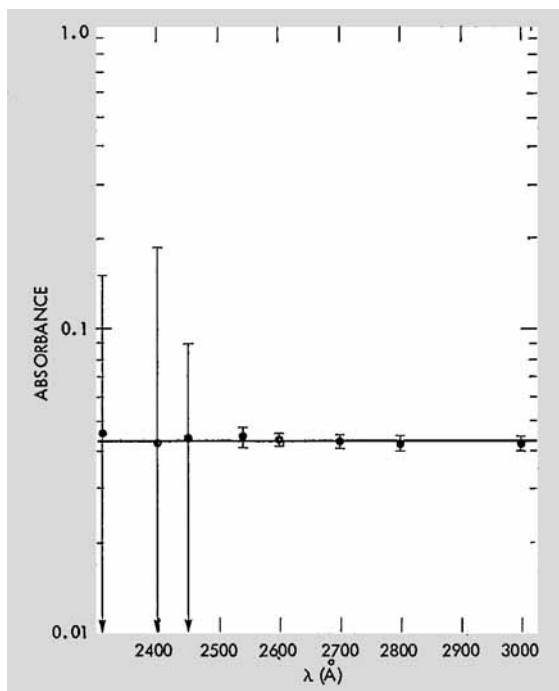


Fig. 3. Reflectance contribution to total absorbance versus wavelength.

a known concentration in a volumetric flask. Error limits are standard deviations from the average.

The absorptivity values for the monomer represent averages over aliquots of at least two separate monomer solutions. In some cases each aliquot

was scanned twice. Four different concentrations of monomer in heptane were used. Error limits are standard deviations from the average.

For the monomer-free films the following procedure was used. The ultraviolet spectrum was obtained for each film, and the absorbances at each wavelength of interest were plotted against the thicknesses in units of moles per square centimeter of the various polymer films. Eleven films in the thickness range from 4.8×10^{-6} to 1.8×10^{-5} mol cm⁻² were used to obtain data in the wavelength range 2200–2400 Å, and an additional eleven films in the thickness range from 1.4×10^{-5} to 7.1×10^{-5} mol cm⁻² were used to extend the wavelength range to 3000 Å. The linear plots so obtained were extrapolated back to zero thickness by use of a nonweighted, linear, least-squares fit to yield the reflectance losses at the film surfaces. Along with the reflectance correction, the least-squares analysis gave the absorptivity value at each wavelength and the standard deviation in the absorptivity and in the reflectance. These are the values included in column 6 of Table I, where error limits are shown, except for the values at 2200, 2250, 2350, and 2537 Å, which represent arithmetic averages and standard deviations from these averages. The remaining entries in column 6 are arithmetic averages obtained from the same films.

In Figure 2 are shown typical plots of absorbance versus film thickness for both the monomer-free films and films obtained from the 90°C bulk polymer. Extrapolation to zero thickness yields the reflectance correction. In Figure 3 the reflectance contribution is plotted as a function of wavelength. The constant value of the reflectance contribution is in agreement with the fact that for most colorless organic compounds, such as the polymer used here, the refractive index does not vary greatly as a function of wavelength in the ultraviolet range.¹⁵

FILMS CAST FROM BULK POLYMER SOLUTIONS

From Figure 1 it can be seen that the methyl methacrylate monomer has absorptivity values up to an order of magnitude greater than the pure polymer. When the bulk PMMA was cast into films, the absorptivities decreased by a factor of 2 or more. This decrease could have been due to either or both of two effects: (1) a shift in the spectrum from one phase to another and (2) a loss of some residual monomer during the casting and subsequent heating and evacuating process.

To estimate the magnitude of the first effect, the absorptivity values obtained from a number of films cast from a solution of the bulk polymer were compared with the absorptivity values obtained after the same films were dissolved in CH₂Cl₂ and the solution absorbances had been determined. The absorptivities from both the films and film solutions fell within each others' error limits at each wavelength of interest, and therefore it was assumed that spectral shifts due to the change in phase were insignificant, if not absent completely.

The second effect might be expected, since methyl methacrylate has an appreciable vapor pressure even at room temperature. A test was carried

out in which a known percentage by weight of the monomer was added to a methylene chloride polymer solution and a film was then cast from this solution. The absorbance at various wavelengths showed a large, initial loss of monomer taking place during the casting process. The film was then heated at approximately 80°C under vacuum for a total of 48 hr. At 8 hr intervals the film was allowed to cool, and its absorption spectrum was measured. Essentially no change in the absorbance was noted, which indicated that the significant loss of monomer took place only as the film was being formed.

From Figure 2 it can be seen that the bulk films showed much more scatter in their absorbance values than did the monomer-free films. It would seem that varying and unreproducible amounts of the monomer are removed during the casting process. Similar observations have been made by Basile¹⁶ regarding styrene monomer in polystyrene samples. But once the films are cast, mild heat treatments will not alter the monomer content. Furthermore, it has been observed that heating films of the monomer-free PMMA under vacuum at 80°C for 24 hr did not result in the formation of observable amounts of monomer.

Measurements on Solutions

Consider first the situation wherein the unknown sample is dissolved in an appropriate solvent, such as methylene chloride, and the absorption spectrum is determined in the range 2400–2600 Å. Then

$$A(\lambda)/b = C_M a_M(\lambda) + C_P a_P(\lambda) \quad (2)$$

The subscripts M and P refer, respectively, to monomer and polymer; C is the concentration:

$$C_P = W_P/M_P V \quad C_M = W_M/M_M V$$

Here M_i = molecular weight of i th species, and W_i = weight of i th species in total volume V . We shall take $M_M = M_P$, since we shall be concerned only with weight fractions. Thus, M_P refers to the weight of one unit in the polymer chain and not the actual molecular weight. Therefore,

$$A(\lambda)/b = (1/M_M V) [W_M a_M(\lambda) + W_P a_P(\lambda)] \quad (3)$$

If we define $W_{M+P} = W_M + W_P$, then

$$A(\lambda)/b = (W_{M+P}/M_M V) [(W_M/W_{M+P}) a_M(\lambda) + (W_P/W_{M+P}) a_P(\lambda)] \quad (4)$$

But $\omega_i = W_i/W_{M+P}$ is the weight fraction of the i th species, and $W_{M+P}/M_M V = C_{\text{eff}}$, or the effective concentration of the solution. We now obtain

$$A(\lambda)/b = C_{\text{eff}} [\omega_M a_M(\lambda) + \omega_P a_P(\lambda)] \quad (5)$$

Let us define the function

$$a(\lambda) = A(\lambda)/b C_{\text{eff}}$$

We obtain finally

$$a(\lambda) = \omega_M a_M(\lambda) + \omega_P a_P(\lambda) \quad (6)$$

If $a(\lambda)$ is measured at two different wavelengths, this equation may be solved exactly for the two weight fractions. However, if $a(\lambda)$ is available at several wavelengths, the least-squares procedure may be employed. A decision must be made as to whether a weighted or an unweighted method should be used, and in the former case as to what the weighting factor should be. In our opinion, the sums of the squares of the residuals should be weighted by $a^{-1}(\lambda)$, because the $a_i(\lambda)$ values vary considerably over the wavelength region of interest. This choice of weighting factor tends to emphasize the $a_i(\lambda)$ values in the middle of the range. However, since this choice of weight factor is really a matter of taste, we shall consider the unweighted procedure as well.

Summing over the values obtained at n different wavelengths, the normal equations of interest are found to be:

Unweighted:

$$\begin{aligned}\omega_M \sum a_M^2(\lambda) + \omega_P \sum a_M(\lambda)a_P(\lambda) &= \sum a(\lambda)a_M(\lambda) \\ \omega_M \sum a_M(\lambda)a_P(\lambda) + \omega_P \sum a_P^2(\lambda) &= \sum a(\lambda)a_P(\lambda)\end{aligned}\quad (7)$$

Weighted:

$$\begin{aligned}\omega_M \sum [a_M^2(\lambda)/a(\lambda)] + \omega_P \sum [a_M(\lambda)a_P(\lambda)/a(\lambda)] &= \sum a_M(\lambda) \\ \omega_M \sum [a_M(\lambda)a_P(\lambda)/a(\lambda)] + \omega_P \sum [a_P^2(\lambda)/a(\lambda)] &= \sum a_P(\lambda)\end{aligned}\quad (8)$$

It can be shown¹⁷ that the weight fractions and their standard deviations σ_i may be obtained from the equations shown in the following two subsections.

Equations from the Unweighted Least-Squares Treatment

$$\omega_M = [\sum a_P^2(\lambda) \sum a(\lambda)a_M(\lambda) - \sum a_M(\lambda)a_P(\lambda) \sum a(\lambda)a_P(\lambda)]/D \quad (9)$$

$$\sigma_M = \pm [\sigma^2 \sum a_P^2(\lambda)/D]^{1/2} \quad (10)$$

$$\omega_P = [\sum a_M^2(\lambda) \sum a(\lambda)a_P(\lambda) - \sum a_M(\lambda)a_P(\lambda) \sum a(\lambda)a_M(\lambda)]/D \quad (11)$$

$$\sigma_P = \pm [\sigma^2 \sum a_M^2(\lambda)/D]^{1/2} \quad (12)$$

$$D = \sum a_M^2(\lambda) \sum a_P^2(\lambda) - [\sum a_M(\lambda)a_P(\lambda)]^2 \quad (13)$$

$$\sigma^2 = \{\sum [a(\lambda)_{\text{obs}} - a(\lambda)_{\text{calc}}]^2\}/(n - 2) \quad (14)$$

Here n is the number of observations made at different wavelengths.

Equations from the Weighted Least-Squares Treatment

$$\omega_M = \{\sum [a_P^2(\lambda)/a(\lambda)] \sum a_M(\lambda) - \sum [a_M(\lambda)a_P(\lambda)/a(\lambda)] \sum a_P(\lambda)\}/D \quad (15)$$

$$\sigma_M = \pm \{\sigma^2 \sum [a_P^2(\lambda)/a(\lambda)]/D\}^{1/2} \quad (16)$$

$$\omega_P = \{\sum [a_M^2(\lambda)/a(\lambda)] \sum a_P(\lambda) - \sum [a_M(\lambda)a_P(\lambda)/a(\lambda)] \sum a_M(\lambda)\}/D \quad (17)$$

$$\sigma_P = \pm \{\sigma^2 \sum [a_M^2(\lambda)/a(\lambda)]/D\}^{1/2} \quad (18)$$

$$D = \sum [a_M^2(\lambda)/a(\lambda)] \sum [a_P^2(\lambda)/a(\lambda)] - \{ \sum [a_M(\lambda)a_P(\lambda)/a(\lambda)] \}^2 \quad (19)$$

$$\sigma^2 = \sum [a(\lambda)_{\text{obs}} - a(\lambda)_{\text{calc}}]^2 / (n - 2) \quad (20)$$

Here n is the number of observations made at different wavelengths.

Measurements on Thin Films

When dealing with thin films of uniform thickness, one often measures the transmittance of the film relative to air. In this case, a correction for reflection losses at the front and back surfaces must be made.

Equation (3) represents the film case if we let b and V be the thickness and volume of the film. Let V_{P+M} be the volume of the film containing some monomer. Then.

$$V_{P+M} = W_{P+M}/1000\rho_{P+M} \quad (21)$$

where ρ_{P+M} is the density of the film. Replacing V in eq. (3) by V_{P+M} yields

$$A(\lambda)/b = (1000\rho_{P+M}/M_M)[\omega_M a_M(\lambda) + \omega_P a_P(\lambda)] \quad (22)$$

If we define the symbol $a'(\lambda)$ as follows, taking a value of 1.179 g cm⁻³ for the density and a value of 100.11 for M_M , then

$$a'(\lambda) \equiv A(\lambda)M_M/1000\rho_{P+M} b = 0.849A(\lambda)/b$$

and we have

$$a'(\lambda) = \omega_M a_M(\lambda) + \omega_P a_P(\lambda) \quad (23)$$

The last expression is identical in form with eq. (6). All eqs. (9) through (20) previously derived by the least-squares treatment for solution data will apply to the film case if one merely replaces $a(\lambda)$ by $a'(\lambda)$.

TABLE III
Smoothed Absorptivity Values for Methyl Methacrylate Monomer^a

$\lambda,$ Å	$a_M(\lambda)$	$\lambda,$ Å	$a_M(\lambda)$	$\lambda,$ Å	$a_M(\lambda)$
2200	2000.0	80	83.9	40	11.85
20	1200.0	2500	77.6	60	9.63
40	690.0	20	70.9	80	7.84
60	388.0	37	66.1	2800	6.39
80	223.0	40	64.1	20	5.18
2300	160.0	60	57.3	40	4.16
20	131.0	80	50.6	60	3.32
40	117.0	2600	43.9	80	2.63
60	111.0	20	37.6	2900	2.11
80	109.0	40	31.8	20	1.74
2400	104.6	60	26.6	40	1.46
20	100.4	80	21.9	60	1.19
40	95.4	2700	17.9	80	0.93
60	89.9	20	14.6	3000	0.79

^a See text for explanation of apparent accuracy of these smoothed values.

TABLE IV
Smoothed Absorptivity Values for Monomer-Free Poly(methyl Methacrylate)^a

$\lambda,$ Å	$a_P(\lambda)$	$\lambda,$ Å	$a_P(\lambda)$	$\lambda,$ Å	$a_P(\lambda)$
2200	179.0	60	41.0	20	0.74
20	166.0	80	30.0	37	0.50
40	146.0	2400	21.0	40	0.42
60	123.0	20	14.2	60	0.26
80	103.0	40	9.3	80	0.154
2300	83.9	60	5.8	2600	0.092
20	67.2	80	3.26		
40	53.4	2500	1.59		

^a See text for explanation of apparent accuracy of these smoothed values.

In order to use eqs. (9) through (20) effectively, it is necessary to know the absorptivities of the monomer-free polymer and of the monomer at quite a few wavelengths in the range 2200–2600 Å. Using a Fourier cosine series curve-fitting program, we have smoothed the values given in Tables I and II and have interpolated to obtain absorptivities in steps of 20 Å. These are listed in Tables III and IV. Note that values are listed with an *apparent* accuracy far beyond that shown in Tables I and II. When using eqs. (9) through (20) it is necessary to carry a very large number of decimal places in the calculations and at the end to round off to the number of decimal places indicated by the standard deviations σ_M and σ_P . Thus the apparent accuracy shown in Tables III and IV is not real but merely reflects an arbitrary rounding off of the numbers obtained from the curve-fitting program. Because of the smoothing produced by the curve-fitting program, however, the values in Tables III and IV are probably more accurate *relative to each other* than are the actual experimental values.

Using the above information, we have computed the monomer concentration in two bulk PMMA samples polymerized at 70 and 90°C, respectively. The monomer concentrations were computed to be $7.5 \pm 0.5\%$ for the former and $3.5 \pm 0.5\%$ for the latter. Figure 4 compares the experimental absorptivities for the 90°C bulk polymer, measured in solution, with the values calculated assuming 3.5% of the monomer to be present.

A valid question may be raised, however, about the appropriateness of the least-squares approach outlined above. In eq. (6) the restriction that $\omega_M + \omega_P = 1$ was not used. The weight fractions were treated as independent constants. Only if the input data $a_M(\lambda)$ and $a_P(\lambda)$ were reasonably good would we expect to find that the weight fractions sum to unity within the error limit $(\sigma_M^2 + \sigma_P^2)^{1/2}$. We have examined only two types of bulk polymer, samples polymerized at 70 and 90°C. Additional systems should be studied to check the reliability of the $a_M(\lambda)$ and $a_P(\lambda)$ values reported here.

Although in the two bulk polymers studied here the weight fractions did sum to unity, supporting the use of the least-squares treatment, in some

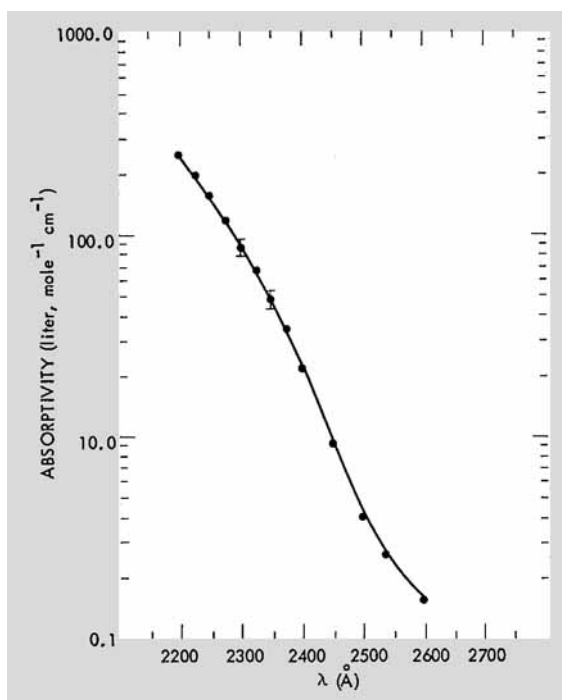


Fig. 4. Comparison of experimental and calculated absorptivities for bulk PMMA, assuming 3.5% residual monomer.

cases it might be desirable to force this condition by introducing the restriction directly into eq. (6). Then

$$a(\lambda) = \omega_M [a_M(\lambda) - a_P(\lambda)] + a_P(\lambda) \quad (24)$$

The average value $\bar{\omega}_M$ is given by

$$\bar{\omega}_M = (1/n) \sum [a(\lambda) - a_P(\lambda)] / [a_M(\lambda) - a_P(\lambda)] \quad (25)$$

The variance is then

$$\sigma_M^2 = [1/(n-1)] \sum_{i=1}^n [(\omega_M)_i - \bar{\omega}_M]^2 \quad (26)$$

As before, n equals the number of observations made at different wavelengths.

We have found that this last approach produced estimates of the weight fraction of monomer that agreed, well within the error limits, with the least-squares estimates.

CONCLUSION

It would appear that ultraviolet absorption spectra can be used to determine fairly accurately residual monomer of 1% or more in polymer samples.

Such determinations would best be made at wavelengths in the range 2400–2600 Å, since in this range the difference between the monomer and polymer absorptivities is the greatest. The spectrophotometric technique has been used before, to determine residual monomer in polystyrene¹⁸ and to determine styrene in a styrene–methyl methacrylate copolymer,¹⁹ for example. We feel, however, that the smoothed absorptivities presented here are accurate enough to warrant the use of the least-squares approach, with its inherently more meaningful error analysis.

This work was performed in part under the auspices of the U.S. Atomic Energy Commission.

The authors are pleased to acknowledge the assistance of G. Henry in determining the residual solvent in the polymer films by a neutron activation analysis technique and of D. Ward in obtaining some ultraviolet spectra of the bulk polymers in solution. The curve-fitting program was kindly supplied by D. Freeman.

References

1. H. W. Melville, *Proc. Roy. Soc. (London)*, **163A**, 511 (1937).
2. J. W. Goodeve, *Trans. Faraday Soc.*, **34**, 1239 (1938).
3. A. Katchalsky and H. Wechsler, *J. Polymer Sci.*, **1**, 229 (1946).
4. P. Cowley and H. Melville, *Proc. Roy. Soc. (London)*, **210A**, 461 (1952).
5. J. Halsam, S. Grossman, D. Squirrell, and S. Loveday, *Analyst*, **78**, 92 (1953).
6. P.-O. Kinell, *A Spectrophotometric Study of Polymethyl Methacrylate*, Almqvist and Wiksells, Boktryckeri AB, Uppsala, 1953.
7. A. R. Shultz, *Phys. Chem.*, **65**, 967 (1961).
8. R. Fox, S. Isaacs, and S. Stokes, *J. Polymer Sci. A*, **1**, 1079 (1963).
9. M. D'Alagni, P. De Santes, A. Liquori, and M. Savino, *J. Polymer Sci. B*, **2**, 925 (1964).
10. J. Kroh, *Roczniki Chem.*, **31**, 175 (1957).
11. H. Bauer, *Plaste Kautschuk*, **2**, 197 (1955).
12. P. Kinell, *Arkiv Kemi*, **14**, 353 (1959).
13. D. M. Wiles and S. Bywater, *J. Polymer Sci. B*, **2**, 1175 (1964).
14. H. H. Jaffe and M. Orchin, *Theory and Application of Ultraviolet Spectroscopy*, Wiley, New York, 1962.
15. N. Bauer and S. Lewin, *Techniques of Organic Chemistry*, Vol. I (*Physical Methods of Organic Chemistry*, Part II), Interscience, New York, 1960, p. 1150.
16. L. Basile, *J. Chem. Phys.*, **36**, 2204 (1962).
17. O. L. Davies, *The Design and Analysis of Industrial Experiments*, Hafner, New York, 1963.
18. J. E. Newell, *Anal. Chem.*, **23**, 445 (1951).
19. A. V. Tobolsky, A. Eisenberg, and L. O'Driscoll, *Anal. Chem.*, **31**, 203 (1959).

Received April 2, 1968