other data for times greater than 10^{-3} sec. by multiplying the values of log I/I^0 by factors of -2.71 and -2.08, respectively. These adjusted data, which are plotted on Fig. 6, depart widely from the other data and the curve ($x + y$ *vs.* t) at times less than 8×10^{-4} sec. The dotted curve is a plot of y *vs.* t, calculated using the parameters selected to fit data corresponding to λ 4680 Å. The general agreement between this dotted curve and the data corresponding to λ 5245 Å. is consistent with the assumed mechanism and the special postulate that the observed increase in absorption is due entirely to the secondary photo-product, G. In other words $\bar{\alpha}_{GH'} \simeq \alpha_1$ and $\bar{\alpha}_G \simeq \alpha_2$, at λ 5245 Å. An experiment performed with light whose wave length band centered at 6810 Å. showed no change in transmissivity upon illumination, presumably indicating that none of the substances present absorb appreciably at this wave length.

A slightly modified mechanism, in which step 4 is replaced by the simple unimolecular step, $GH' \rightarrow GH$, $-v_{4A} = k_{4A}(GH')$, is also compatible with the results of the flash experiments. This mechanism leads to the differential equations

$$-\,dx/dt = [k_{4A} + k_{5i}(O_{x_i})]x$$
$$-\,dy/dt = k_{6i}my^2 - k_{5i}(O_{x_i})x$$

Acceptable values for the parameters corresponding to this mechanism are: $x_0 = 0.65$, $y_0 = 0.15$, $k_{4A} = 3.5 \times 10^3$ sec.$^{-1}$, $k_{5i}(O_{x_i}) = 1.5 \times 10^2$ sec.$^{-1}$ and $k_{6i} = 3.1 \times 10^9 m^{-1}$ sec.$^{-1}$. The agreement between the experimental data and the curve, derived from these equations and parameters, is somewhat inferior (especially during the first half of the reaction) to that illustrated by Fig. 6 for the preceding mechanism.

Steps 7, 8 and 9 are introduced to take into account the effect of oxygen upon the steady-state[3d] and flash reversible "bleaching" and on the slow irreversible bleaching.[3d] The bimolecular step 8, rather than a first-order dissociation of the complex $GH\cdot O_2$, is indicated by Gaffron's[12] quantitative measurements of chlorophyll-sensitized autoöxidation. Values for the rate constants of these reactions, which are consistent with the constants of the preceding steps, and which appear to be compatible with all of the available pertinent data, are as follows: $k_7 = 2.7 \times 10^{10}$, $k_8 = 1.4 \times 10^{10}$ and $k_9 = 8 \times 10^5 m^{-1}$ sec.$^{-1}$.

Since all of the experiments under discussion were performed in methanol, or similar activating solutions,[13] the normal chlorophyll molecule, represented here as GH, is the one-to-one addition compound of chlorophyll and a basic solvent. The present evidence does not preclude the stabilization of an intermediate radical by the loss or gain of a proton, as has been suggested by Terenin.[14] For example, it is possible that step 5 is the result of an electron transfer followed by a rapid equilibrium

$$O_{xi} + GH' \longrightarrow O_{xi}^- + GH^+$$
$$MeOH + GH^+ \rightleftharpoons MeOH_2^+ + G$$

For sake of simplicity, such possibilities are not considered here.

[12] H. Gaffron, *Ber.*, **60**, 755 (1927).

[13] R. Livingston, W. Watson and J. McArdle, THIS JOURNAL, **71**, 1542 (1949); R. Livingston and S. Weil, *Nature*, **170**, 750 (1952).

[14] A. Terenin, *Bull. acad. sci. U.R.S.S. ser. biol.*, 369 (1947).

MINNEAPOLIS, MINNESOTA

[E. I. DU PONT DE NEMOURS & CO. EXPERIMENTAL STATION POLYCHEMICALS DEPARTMENT]

A New Apparatus for Rate Studies Applied to the Photopolymerization of Methyl Methacrylate

BY M. A. NAYLOR AND F. W. BILLMEYER, JR.

RECEIVED NOVEMBER 7, 1952

An apparatus is described which permits a reasonably accurate study of the rate of reaction by following refractive index changes. Certain results obtained on the polymerization of methyl methacrylate are given.

Introduction

This paper describes a new apparatus for following the rate of a reaction and presents certain data obtained some time ago in a study of the photocatalyzed polymerization of methyl methacrylate. In many bulk polymerizations, the reaction mixture passes through a viscous stage and finally to a solid. It is particularly difficult to follow the rates of reaction in these high conversion regions by dilatometric or precipitation techniques. Experimental difficulties accompanying operations with "gelled" systems make sampling and the usual kinetic measurements extremely troublesome. This equipment should be useful in following the course of any reaction accompanied by a significant change in refractive index and occurring in a homogeneous liquid system.

The apparatus described here has been termed an "oblique-line refractometer" and it has proved operable over the range of 0 to 100% conversion with methyl methacrylate. This equipment was designed to operate with actinic light; however, other modifications have been used in this Laboratory to study thermal polymerizations.

Polymerizations were carried out using benzoin or 2,2′-azo-bis-isobutyronitrile as photocatalysts with light primarily in the 3600 Å. region. As might be expected, the kinetics in such a system are identical with those of polymerizations employing thermal catalysts except for differences attributable to the method of forming chain initiating radicals. These latter differences result in several interesting effects which, however, are in agreement with the generally accepted mechanism of vinyl polymerization.[1]

[1] (a) R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942); (b) K. S. Bagdasar'yan, *J. Phys. Chem.* (*U.S.S.R.*), **21**, 25 (1947); (c) G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947); (d) E. Trommsdorff, *et al.*, *ibid.*, **1**, 169 (1948); (e) M. S. Matheson, *et al.*, THIS JOURNAL, **71**, 497 (1949).

Experimental

Oblique-line Refractometer.—Rate studies were carried out by following the change in the refractive index of the polymerization mixture as the reaction progressed. This was done by following the change in the position of the image of an illuminated slit placed at an angle behind a cylindrical tube containing the reaction mixture. A discussion of the refractive index of matter in cylindrical form has been given by Pfund, and the principles which he proposed were utilized in this apparatus.[2]

Figure 1 shows a schematic diagram of the oblique-line refractometer. The equipment consisted of a constant temperature bath made in the form of a box of Lucite acrylic resin approximately 5″ × 6″ × 12″ in size. A sheet of Corex D glass (Corning #9700, Corning Glass Co., Corning, N. Y.) formed the front window of the bath and allowed good transmission of the actinic light. The oblique lines, L, were made by milling 0.007″ slits $^1/_2$″ apart at a 45° angle to horizontal into a sheet of $^1/_8$″ brass. The brass sheet with the slits was mounted vertically in the middle of the constant temperature bath parallel to the glass front. A frame of Lucite equipped with fuse clips at the top and bottom was used to hold 7 mm. diameter Pyrex reaction tubes, T, in a vertical position. The apparatus would hold a total of ten reaction tubes.

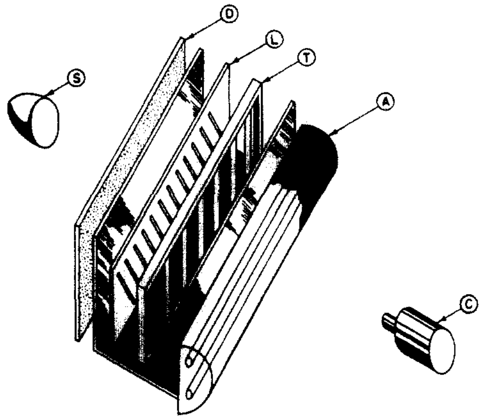

Fig. 1.—Diagram of oblique line refractometer.

The position of the image of the oblique lines in the reaction tube and the sensitivity of measurement depend upon the refractive indices of the bath and reaction tube, the angle which the oblique line makes with the reaction tube, and the distance between the reaction tube and the oblique line. It was found that by using a water–ethylene glycol-bath with the refractive index adjusted to 1.3909 at 25°, adequate sensitivity over the whole range of conversion could be obtained. The reaction tubes were placed in the constant temperature bath 1.7″ in front of the brass plate containing the oblique slits.

The ultraviolet light source consisted of a Dazor desk lamp fixture A, (Dazor Mfg. Co., St. Louis, Mo.), mounted across the front of the refractometer to give uniform illumination on all ten reaction tubes. With two 15-watt General Electric BL-360 fluorescent bulbs in this fixture, a field of illumination 12″ × 4″ was obtained which showed maximum intensity variations of 1% at different positions in the field. This factor was also checked by running several identical polymerizations at different positions in the tube rack, and in all cases the rates were identical. The low temperature of operation, uniform field of illumination, and relatively intense 3600 Å. radiation made this light source quite suitable for this work.

Readings of the angle between the oblique slit and its image in the reaction tube (which can be calibrated in terms of per cent. polymerization) were made by photographing the tubes and slits at timed intervals during the course of the reaction. Illumination for photographing was furnished by a flood lamp, S, mounted behind a diffusing screen, D, placed to the rear of the bath and oblique lines. Photographs were taken with a Leica camera, C, mounted in a copying attachment placed in front of the bath. Since the ultraviolet source was between the camera and bath, it was necessary to raise the Dazor fixture when pictures were taken. This operation required about 0.5 minute during which time irradiation of the samples was stopped.

Measurements of the angles were made with a protractor after projecting the negatives onto a 12″ × 12″ screen. Such measurements were accurate to ±2% polymer.

A refinement in the reading device was made by installing a cross-hair reticle in the eyepiece of a Schmidt and Haensch polarimeter. This device was mounted in place of the camera, and observation of the image angle could be made directly from the calibrated polarimeter scale. Angles so measured were reproducible to ±0.5% polymer, but, since this device was applicable to only one determination at a time, it was used very little. In view of the large number of separate determinations which we wished to make, the photographic method was considered to be most useful.

A photograph illustrating the type of image obtained with this apparatus is given in Fig. 2. In this picture the lowest degree of reaction is in the tube on the left (25% conversion) and the highest degree is on the right (58% conversion).

A calibration curve relating the angle between the oblique slit and its image in the reaction tube to percentage polymerization was prepared from standard solutions of polymer in monomer. A total change in angle measured of 83° was obtained in going from pure monomer to 100% polymer.

While this technique is not so precise as certain other kinetic methods, it is especially useful since it enables one to measure the rate of bulk polymerization in homogeneous systems even when the material is in a gel or solid state. Some difficulty was experienced at high conversions when rates were unusually fast because polymer tended to pull away from the tube walls giving a distorted image.

Preparation of Reaction Tubes.—Freshly fractionated methyl methacrylate obtained from the du Pont Arlington Plant was used. In one set of determinations, the monomer was redistilled under high vacuum, and another portion was merely swept thoroughly with purified nitrogen, frozen, and sealed off under vacuum. Identical results were obtained from the above procedures so the latter was adopted for most of the experiments.

The tubes in which the polymerizations were carried out were made by sealing off 8″ lengths of 7 mm. Pyrex brand tubing at one end. These were "necked down" 6″ from the sealed end and were filled with 2 ml. of monomer containing catalyst. After the monomer was swept for three minutes with purified nitrogen introduced through a fine capillary, it was frozen in Dry Ice–methanol and evacuated to a pressure of less than 1 mm. The tube was then sealed at the "necked down" point.

Tubular Reactor.—This type of reaction vessel was used to prepare larger quantities of polymer for investigation of the properties of the polymer formed during the early stages of the polymerizaton. Reactions were carried only to about 25% conversion to prevent the reaction mixture from setting to a solid. The reaction vessel consisted of a 50 mm. Pyrex brand tube about 20″ long sealed at one end and surrounded with a vacuum jacket. The vacuum jacket was necessary only for low temperature work to prevent frost formation on glass surfaces located between the light source and the reaction mixture. A U-tube of 6 mm. tubing was used as a cooling coil. The top of the reaction tube was fitted with a rubber stopper through which the cooling coil, thermocouple and nitrogen inlet tube passed. Two 15-watt Dazor fixtures were mounted on opposite sides of the reactor. Nitrogen was bubbled continuously through the polymerizing mixture to exclude air and to maintain agitation. Polymerizations from −60 to +92° were carried out in this reactor. Chilled or warmed water was used to maintain the temperature above 5° and methanol pumped through a Dry Ice–methanol-bath to maintain temperatures below 5°.

Polymer was isolated from the sirups by precipitation with methanol. After precipitation, the polymer was redissolved in acetone and reprecipitated in very fine granular form by the addition of methanol with violent shaking. The polymer was then filtered and dried at 80° for 5 hr. All the polymer tested was granulated from an acetone solution as described above.

Measurement of Molecular Weight and Molecular Weight Distribution Breadth.[3]—Molecular weights were

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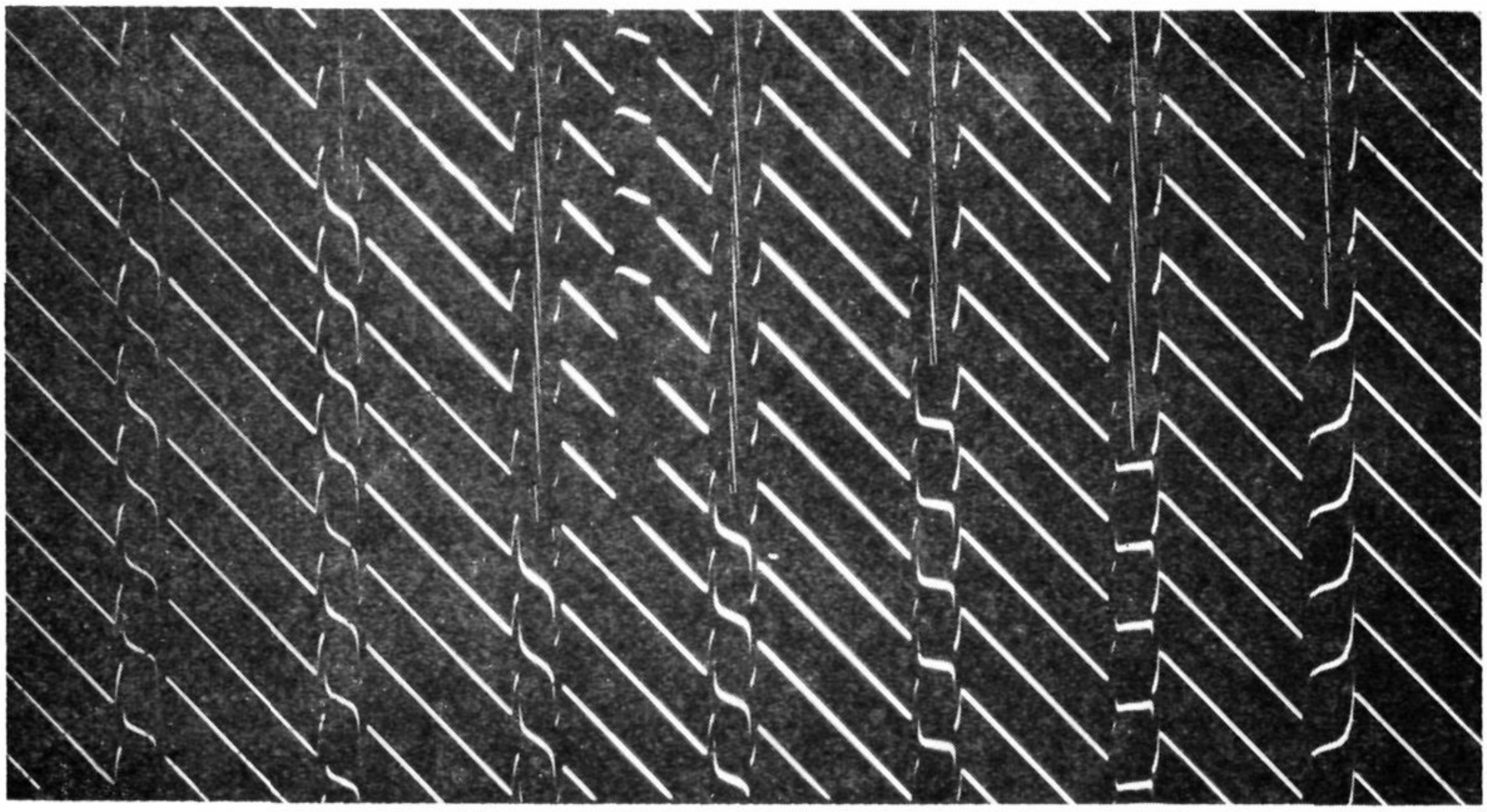
[2] A. H. Pfund, *J. Optical Soc. Am.*, **30**, 410 (1940).

[3] These measurements were made by Miss A. M. Trzcinski.



(25% Conversion). (58% Conversion).

Fig. 2.—Photograph of reaction tubes in oblique line refractometer.

measured by the viscosity method, using modified Ostwald viscometers at 25°. Ethylene dichloride and chloroform were used as solvents. Corrections for kinetic energy and shear rate were found to be insignificant; efflux times for the solvents were over 100 sec. For each solvent the Huggins constant k^1 was near 0.33 and the intrinsic viscosity was estimated by the equation[4]

$$[\eta] = (\sqrt{2\eta_{\mathrm{sp}} - 2 \ln \eta\, r})/C$$

Molecular weights were calculated from the equations $Mw = 3.8 \times 10^5 [\eta]^{1.3}$ for ethylene dichloride and $Mw = 3.5 \times 10^5 [\eta]^{1.3}$ for chloroform. These equations have been established through light scattering measurements made in this Laboratory.

Measurements of molecular weight distribution breadth were made by the summative fractionation method developed in this Laboratory and described elsewhere.[5] In this paper the results were expressed in terms of the weight to number average molecular weight ratio Mw/Mn.

Discussion of Results

Rate Curves.—Several rate curves are given in Fig. 3. They illustrate the normal shape of the rate curve for the bulk polymerization of methyl methacrylate and have been observed and interpreted by other workers.[1,6]

It was shown that isothermal conditions (±0.5°) were maintained by sealing a thermocouple into one of the reaction tubes and following the internal temperature through the most rapid part of a run.

The curve for a first-order dependence of rate upon monomer concentration was calculated from the initial portion of the observed rate curve at 20° and is included in Fig. 3. The following equation was found to explain the results obtained to a first approximation.

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_2[\mathrm{M}]\left(\frac{(k_1[\mathrm{cat}]I}{k_3}\right)^{1/2}$$

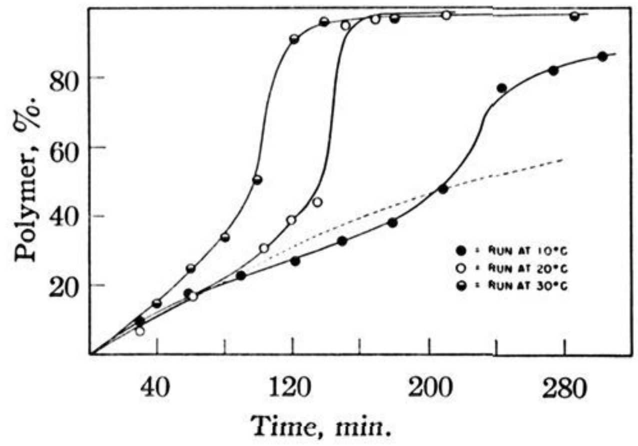


Fig. 3.—Effect of temperature on rate of photopolymerization of MMA (0.2% benzoin). The dotted curve is the theoretical first-order rate curve calculated using the initial observed rate constant for the run at 20°.

where

[M] = monomer concentration
k_1 = rate constant for chain initiation
k_2 = rate constant for chain propagation
k_3 = rate constant for chain termination
[cat] = catalyst concentration
I = light intensity.

Effect of Conversion.—Significant deviation from the first-order rate curve in Fig. 3 is noted at about 25% conversion with the experiment carried out at 20°. Since isothermal conditions were maintained, the hypothesis that the increase in rate is caused by a decrease in chain termination seems most likely. If this is the case, it is apparent that molecular weight should increase markedly in the region of the rate "take-off." This effect is illustrated in Fig. 4.

The observed change in molecular weight with conversion should lead to a much broader molecular weight distribution in polymerizations taken to high conversion than in polymerizations stopped during the first stages (up to 20% conversion). To check this point distribution breadth measurements

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[4] F. W. Billmeyer, Jr., *J. Polymer Sci.*, **4**, 83 (1949).

[5] F. W. Billmeyer, Jr., and W. H. Stockmayer, *ibid.*, **5**, 121 (1950).

[6] (a) G. V. Schulz and F. Blaschke, *Z. physik. Chem.*, **B50**, 305 (1941); (b) R. G. W. Norrish and E. F. Brookman, *Proc. Roy. Soc. (London)*, **171A**, 147 (1939); (c) L. K. J. Tong and W. O. Kenyon, THIS JOURNAL, **67**, 1278 (1945).

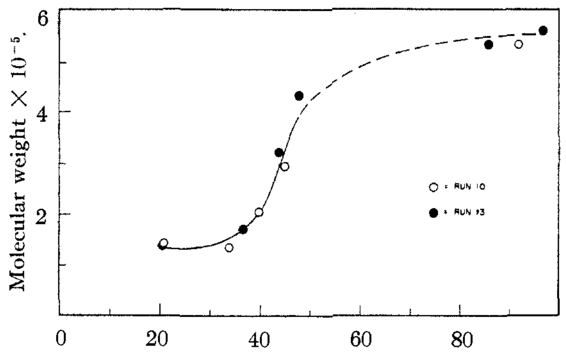

Fig. 4.—Molecular weight of photopolymerized MMA *vs.* conversion (20°, 0.2% benzoin).

were made on the sirup and on a cast sheet made under similar but not identical conditions. The sirup, polymer W[5], had a weight average molecular weight of 180,000 and a ratio of weight to number average molecular weight $Mw/Mn = 2.0$ by summative fractionation. This polymer had an osmotic molecular weight of 98,000 giving directly $Mw/Mn = 1.8$. The cast sheet, polymer E, had a weight average molecular weight of 720,000 and $Mw/Mn = 10$. Similar polymers investigated by others have shown Mw/Mn ratios almost this high.[7]

Effect of Temperature.—The temperature coefficient of the over-all reaction was determined by using the first-order portion of the rate curves (up to 15% conversion) obtained at 8, 20, 30 and 40°. As the temperature increased, the straight portion of the curve was reduced and approached a continuous concave upward appearance to about 80–85% conversion where the sharp decrease set in as usual. Some of these data are shown in Fig. 3. The temperature coefficient for the benzoin-catalyzed reaction in this temperature range was about 1.32/10°, giving an over-all activation energy for polymerization near 5 kcal./mole. This low over-all E_{act} emphasizes the probable importance of diffusion (viscosity) effects.

Several experiments were made in the large tubular reactor described in the experimental section. It was found that the molecular weight increased as the temperature was raised over the range from −27 to +92°, other variables being held constant. Figure 5 illustrates this effect. The increase in molecular weight with temperature indicates that the activation energy of the propagation step is higher than the geometric mean of those for termination and for initiation. If appreciable thermal decomposition of the catalyst were superimposed on the photo reaction, the molecular weight would decrease with increasing temperature at sufficiently high temperatures, as is usually observed with thermally activated catalysts.

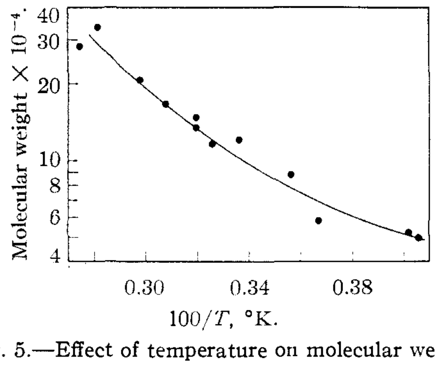

Fig. 5.—Effect of temperature on molecular weight.

Effect of Light Intensity.—Plots of (time) (relative intensity)$^{1/2}$ *vs.* conversion (Fig. 6) showed satisfactory superposition of points in the region of 0 to 30% conversion. Thus, the dependence of rate upon the square root of the light intensity is demonstrated for the initial stages of bulk polymerization. It will be noticed in Fig. 6, however, that a divergence of points at about 30% conversion occurs with the upward curvature being more pronounced at the lower the light intensity. Since this divergence is in the same region as the take-off point of the normal rate curve, it is felt that the divergence is a result of variations in the viscosity of the reaction mixtures. High light intensity produces lower molecular weight material and consequently a lower viscosity at a given conversion. Thus, a higher conversion must be reached at high light intensity before the rapid rate rise is encountered than is required with reduced light intensity. The effect of light intensity on molecular weight is illustrated in Table I.

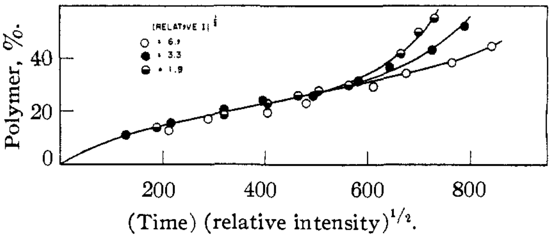

Fig. 6.—Effect of light intensity on rate of photopolymerization of MMA (20°, 0.2% benzoin, 3600 Å. radiation).

Table I

Effect of Light Intensity and Conversion on Molecular Weight of Photopolymerized Polymethyl Methacrylate (0.2% Benzoin, 20°)

Light intensity	Conversion, %	Mol. wt.
Low	18	215,000
Low	90	861,000
High	27	70,000
High	88	260,000

Efforts were made to reduce the rate of polymerization in the region of most rapid reaction, 40–80% conversion. By the introduction of light filters at about 35% conversion, it was found possible to reduce the amount of rate increase to any desired value or to maintain an essentially constant rate over 80% conversion.

Effect of Catalyst Concentration.—The influence of catalyst concentration on rate was quite comparable with the effect of light intensity. This square root dependence would be expected from a

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(7) H. G. Lauterbach, unpublished work at the M.I.T. Plastics Research Laboratory.

mechanism involving absorption of light by the catalyst to produce the chain initiating free radical. The effect of catalyst concentration on the "take-off" point in the rate curve was also comparable to that of light intensity.

Acknowledgment.—The authors wish to thank Dr. A. W. Anderson and Dr. W. H. Stockmayer for many helpful discussions during the course of this work.

WILMINGTON, DELAWARE

[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Stability of Metal Chelates. V. N,N-Dihydroxyethylglycine

BY S. CHABEREK, JR.,[1] R. C. COURTNEY AND A. E. MARTELL

RECEIVED NOVEMBER 11, 1952

The acid dissociation constant and chelate stability constants for the interaction of Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{+2}, Mn^{+2}, Zn^{+2}, Cd^{+2}, Mg^{+2} and Fe^{+3} ions with N,N-dihydroxyethylglycinate ion have been determined by potentiometric *p*H titration measurements. The ligand was found to be less basic than the glycinate ion but showed equal or higher affinity for metal ions, indicating the participation of the hydroxyethyl groups in chelate formation. By means of the titration curves and related information, the divalent metal ions are shown to form chelates with 1 and 2 moles of ligand per metal ion, whereas the 1:1 Fe^{+3} chelate is proved to combine with excess ligand to give a chelate having a ratio of 3 ligands to 2 metal ions. The Fe^{+3} chelates differ from those of the divalent metals in that protons are also displaced from the hydroxyalkyl groups. The chelate stability constants are correlated with the second ionization potential of the metal, and the effect of *p*H on dissociation of the metal chelates is discussed.

Literature reports of the chelating tendencies of amino acids containing auxiliary hydroxyl groups have been limited to a description of N-hydroxyethyliminodiacetic acid given by Chaberek, *et al.*[2] Since this substance was found to have a much greater affinity for transition metal ions than did corresponding compounds without the hydroxyl group, it was concluded that the hydroxyl group is associated with the metal ions, and that the chelating agent is tetradentate. The compound reported in the present paper, containing one amino group, one carboxyl group, and two hydroxyl groups, was first developed by F. C. Bersworth as a special sequestering agent for the Fe^{III} ion,[3] and was kindly donated by him for investigational purposes. Because of its unusual properties, it was believed that special interactions might occur between this chelating agent and certain metal ions.

Experimental

Apparatus and Procedure.—The experimental method used in this investigation is similar to that described in an earlier publication.[4] The temperature was 30 ± 0.05°, and the ionic strength was maintained at 0.10 with KCl. The amino acid concentration was very low—about 2×10^{-3} molar—so that its conversion to other ionic species during the course of the titration would have no more than a negligible effect on the ionic strength. The titration was carried out with potassium hydroxide in a nitrogen atmosphere. Although the *p*H was recorded by a *p*H meter, the values corresponded to *p*H values determined by the hydrogen, silver–silver chloride cell, since the *p*H meter–glass electrode–calomel electrode system was calibrated periodically against the potential of the hydrogen, silver–silver chloride cell with the experimental solution as the electrolyte.

Materials.—The chelating agent, dihydroxyethylglycine was supplied through the courtesy of the Bersworth Chemical Company, Framingham, Mass. Since traces of inorganic salts were present in the original sample—a common impurity in amino acids of this type—it was further purified by successive recrystallizations from rather concentrated aqueous solutions.

Experimental Data.—The experimental measurements which were made are presented graphically in Figs. 1, 2 and 3. The ordinates represent *p*H measurements corrected as described above, and the abscissas are expressed in terms of the quantity *m*, the moles of base added per mole of metal ion in the solution. In Fig. 1 the number of moles of metal was arbitrarily set equal to the number of moles of amino acid present in the solution. Hence in this case *m* is also *a*, the number of moles of base added per mole of amino acid, and the titration curve of the amino acid itself is thus comparable with those of the metal chelates in the same graph. In addition to presentation of the data, these curves serve as evidence for the formulas of the metal chelates formed. Thus it is necessary to study the titration curves before the calculations can be set up for the determination of the stability constants. The reasoning involved in this process is described below in the discussion of results.

Calculations.—The single acid dissociation constant employed for this amino acid is defined by: $k_1 = [H^+][A^-]/[HA]$. The successive metal chelate stability constants are defined by: $K_1 = [MA^+]/[M^{+2}][A^-]$, and $K_2 = [MA_2]/[MA^+][A^-]$. In this paper brackets are employed to designate molar concentration. The calculations of the amino acid dissociation constant, and of the metal chelate stability constants were carried out by the modified Bjerrum method described previously.[4] By this method, the concentration of the anion of the chelating agent $[A^{-1}]$ was calculated algebraically with the aid of the acid dissociation constant. The average number of ligands bound per metal ion was then determined and plotted *vs.* *p*A, (log $1/[A^{-1}]$). The values of *p*A at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ are then equivalent to log K_1 and log K_2, respectively. In practice it was found desirable to calculate log K_1 from titration data for which the concentration of metal ion was equal to the concentration of amino acid, while K_2 was best calculated from measurements on solutions for which the concentration of amino acid was two times that of the metal ion. The dissociation constant of the amino acid was calculated by plotting $\bar{n}$, the number of protons bound per mole of amino acid, *vs.* *p*H, the value of *p*H at $\bar{n} = 0.5$ being equivalent to pk_1.

Hydrolysis of Copper(II) Chelate.—Since the titration curves indicated that the hydroxyl complex of the cupric chelate was formed in the absence of appreciable amounts of other species, the calculation of this equilibrium constant is greatly simplified. If the acid form of the copper(II) chelate is represented by CuA(H$_2$O)$^+$ and the basic

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[1] F. C. Bersworth Postdoctoral Fellow, Clark University.

[2] S. Chaberek, Jr., R. C. Courtney and A. E. Martell, THIS JOURNAL, **74**, 5057 (1952).

[3] The sodium salt of this substance is marketed as a special sequestering agent for trivalent metal ions by the Bersworth Chemical Company, Framingham, Mass. (patent pending).

[4] S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 5052 (1952).