[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Initiation of Polymerization by Di-*t*-butyl Peroxide

BY J. A. OFFENBACH[1] AND A. V. TOBOLSKY

RECEIVED JANUARY 7, 1956

The kinetics of initiation of polymerization by di-*t*-butyl peroxide have been studied in styrene and methyl methacrylate between 60 and 98°. Values of $R_i'/2$ [Cat] determined by these techniques are in excellent agreement with values of $k_d$ obtained in other solvents at higher temperatures by infrared measurements. From determination of an efficiency factor, $f'$, at 70°, it appears that little or no recombination of initiator fragments takes place. The over-all rate law for primary cleavage of the peroxide in solution is given by $k_d = 2.8 \times 10^{14} \exp(-35.0 \text{ kcal.}/RT)$. Reasonable agreement is shown between the solution data and gas phase data extrapolated from higher temperatures.

## Introduction

One of the most stable and inert organic peroxides known at the present time is di-*t*-butyl peroxide. However, the kinetics of the decomposition of this substance have been studied over a wider range of experimental conditions than most peroxides. A simple unimolecular cleavage has been demonstrated both in the gas phase[2-7] and in solution.[8] A summary of the results obtained by various workers and a discussion of reaction mechanism is to be found in a recent monograph on organic peroxides.[9]

Since such detailed studies on unimolecular reactions are not too prevalent in the literature, it was considered desirable to use the technique of initiation of polymerization to furnish more data on the decomposition in various solvents. We have been able, using this technique, to work in a lower temperature range than has previously been investigated. A further advantage lies in the fact that it is not necessary to proceed to high degrees of decomposition to obtain accurate information.

From another point of view, there has been current interest shown in the kinetics of initiation of vinyl polymerization by various free radical sources.[10] Comparison of results obtained for an initiator by polymerization methods with values obtained by other techniques and in other media should be of importance in demonstrating the value of polymerization reactions in measuring the rates of decomposition of free radical sources and in interpretation of the mechanisms of these processes.

## Experimental

**Materials.**—Styrene, Brothers Chemical Company, was given a distillation through a one plate column, equipped with a Newman stopcock, for removal of fractions. At any particular pressure, the middle cut boiling in a 0.2° temperature range was removed for further use in polymerization measurements. Distillation was carried out in a nitrogen atmosphere of about 18 mm., and a boiling point of about 43° was attained by means of a water aspirator. The desired sample was placed immediately under refrigeration till use within one day after removal of inhibitor.

**Methyl methacrylate**, Rohm and Haas, was treated in a separatory funnel with 5% aqueous sodium hydroxide three times in order to remove inhibitor (hydroquinone), followed by three aqueous washes. After drying with anhydrous sodium sulfate for at least six hours, the monomer was distilled through a similar apparatus as used for styrene. Pressure regulation was necessary in conjunction with the use of the water-pump to maintain the boiling range around 40°, and a mercury cut-off manostat was used for this purpose. A middle cut boiling in a 0.2° range was removed for further use, and placed under refrigeration. Samples were used within one day after distillation.

**Benzene**, Mallinckrodt, Analytical Grade, was used without further purification.

**Chloroform**, Mallinckrodt, Analytical Grade, was used without further purification.

**2,2-Diphenyl-1-picrylhydrazyl** (DPPH), Monsanto research sample, was used as received, since the absorption curve was identical with that obtained from a sample of DPPH prepared in this Laboratory and recrystallized from ether-chloroform.

**Di-*t*-butyl peroxide** (DTBP), Lucidol, was purified by passing it through a column two feet long and one half inch in diameter, which had been charged with absorption alumina, Fisher Scientific Company. Further purification was effected by two successive tube-to-tube distillations on a high vacuum manifold from room temperature to liquid air temperature. In each distillation, only the middle cut was used. This procedure was required as the untreated peroxide was found to decolorize a degassed, vacuum sealed solution of DPPH in benzene within 20 minutes at room temperature. Since DPPH is such a stable material at room temperature, it was thought that this loss of color was due to *t*-butyl hydroperoxide, one of the chief impurities in the manufacture of DTBP.[11] Two cc. of *t*-butyl alcohol, when added to a benzene solution of DPPH and subjected to the degassing treatment, caused no visible loss of color, whereas one drop of *t*-butyl hydroperoxide in a similar experiment caused almost instantaneous fading of color. It is important to remove all extraneous materials which could react with DPPH, since the intensity of color is strongly dependent on its concentration, and it has a high molecular weight. Analyses for hydroperoxide were performed by an iodometric procedure of Wagner, Smith and Peters.[12]

**Procedure.**—Polymerizations were carried out in a conventional manner by sealing off, *in vacuo*, Pyrex ampoules containing solutions of di-*t*-butyl peroxide in monomer, after degassing three times. Temperature regulation during the polymerization was within ±0.03°. At the completion of the requisite conversion of monomer, the tubes were removed from the baths, and the polymer formed was precipitated in a tenfold excess of methanol, filtered, dried and weighed. In expressing rates of polymerization and catalyst and monomer concentrations, density corrections have been applied to refer to the chosen working temperature. In addition, the monomer concentrations have been corrected for the presence of liquid catalyst, assuming ideal

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(1) This article is based upon a dissertation submitted by Jack A. Offenbach in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(2) N. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

(3) J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948).

(4) J. Murawski, J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, **19**, 698 (1951).

(5) M. T. Jaquiss, J. S. Roberts and M. Szwarc, THIS JOURNAL, **74**, 6005 (1952).

(6) F. P. Lossing and A. W. Tickner, *J. Chem. Phys.*, **20**, 907 (1952).

(7) G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1425 (1954).

(8) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 336 (1948).

(9) A. V. Tobolsky and R. S. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

(10) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

(11) U. S. Patents 2,383,919; 2,395,523; 2,403,758; 2,403,771; 2,403,772; 2,434,888; 2,446,797 (to Shell Development Company).

(12) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

mixing. Rates are expressed in units of moles/l./sec. and concentrations in moles/l.

Molecular weights were determined using an Ubbelohde viscometer, equipped with a dilution bulb. Intrinsic viscosities were converted to molecular weight values by means of the following relations

(1) Methyl methacrylate in chloroform at 25°[13]

$$\log \bar{P}_n = 3.2485 + 1.250 \log [\eta] \qquad (1)$$

(2) Styrene in benzene at 30°[14]

$$\log \bar{P}_n = 3.2004 + 1.3699 \log [\eta] \qquad (2)$$

$\bar{P}_n$ is a number average degree of polymerization, and $[\eta]$ is the intrinsic viscosity, expressed in deciliters per gram.

Disappearance of color of DPPH was followed using a Fisher Spectrophotometer with the 650 mμ filter inserted in the light beam. A Beer's law relationship was obtainable with the use of the "C" setting of the lamp intensity selector.

## Results

Rates of initiation, $R_i'$, may be calculated from experimentally determined quantities as[10]

$$\frac{R_i\,(1 + x)}{2[\text{Cat}]} = \frac{R_i'}{2[\text{Cat}]} = A'K^2 \qquad (3)$$

The quantity $A'$ is a function only of the particular monomer and the temperature of reaction. In the absence of chain transfer to the initiator, it can be obtained from the slope of the reciprocal number average degree of polymerization *vs.* the rate of polymerization, $R_p$. $K^2$ has been determined from a linear plot of $R_p{}^2$ *vs.* $[M]^2$ [Cat].[15] The monomer concentration is designated as [M], and the initiator concentration by [Cat]. Reference will be made in the Discussion section to $x$, which is the fraction of polymer chains terminating by a disproportionation mechanism.

Values of $R_i'/2$ [Cat] have been determined for initiation of polymerization in styrene at temperatures of 60, 70, 80 and 90°, and in methyl methacrylate at 70 and 98°. A typical linear plot of $R_p{}^2$ *vs.* $[M]^2$ [Cat] is shown in Fig. 1 for methyl methacrylate at 70°. Since DTBP is only a moderately active initiator below 100°, it is not valid to neglect the purely thermal rate of polymerization, and so thermal rates were also determined at each reaction temperature. Values of $A'$ for styrene were calculated from the equation of Tobolsky and Offenbach.[16] This latter equation is obtained from a very satisfactory Arrhenius plot of $A'$ values over a wide temperature range. For methyl methacrylate at 70°, the value of $A'$ reported by Schulz and Harborth[17] was taken, and its value at 98° was determined in this Laboratory. The value of 16.4 obtained was found to coincide exactly with that calculated from the equation of Tobolsky and Baysal.[10] A plot of $1/\bar{P}_n$ *vs.* $R_p$ at 98° is given in Fig. 2.

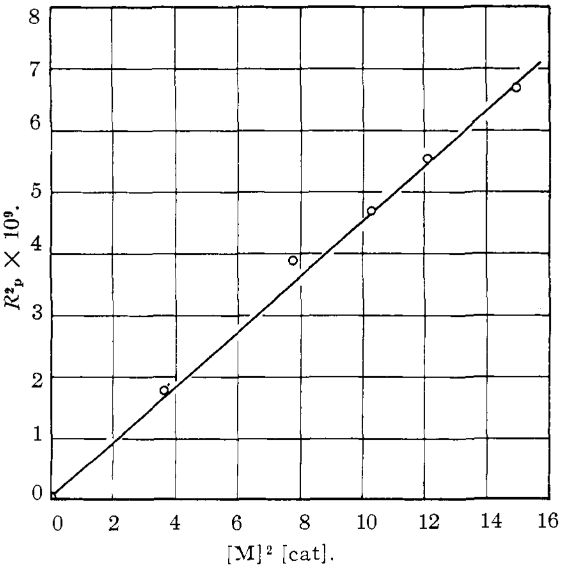

Fig. 1.—Methyl methacrylate-DTBP at 70°.

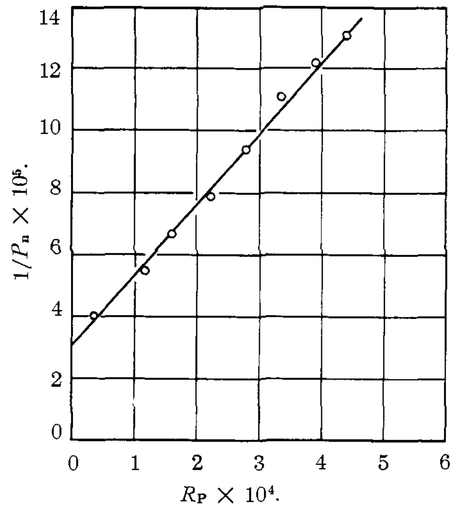

Fig. 2.—Methyl methacrylate-DTBP at 98°.

Magnitudes of the slopes, $K^2$, and thermal rates, as well as calculated values of $R_i'/2$ [Cat] are presented below in Table I.

TABLE I

STYRENE POLYMERIZATION

| $T$, °C. | $K^2$ | $R_p$, thermal | $R_i'/2$[Cat] | log $R_i'/2$ [Cat] |
|---|---|---|---|---|
| 60 | $3.77 \times 10^{-12}$ | $2.08 \times 10^{-6}$ | $3.22 \times 10^{-9}$ | −8.492 |
| 70 | $2.83 \times 10^{-11}$ | $4.70 \times 10^{-6}$ | $1.44 \times 10^{-8}$ | −7.847 |
| 80 | $1.92 \times 10^{-10}$ | $1.11 \times 10^{-5}$ | $5.65 \times 10^{-8}$ | −7.248 |
| 90 | $1.43 \times 10^{-9}$ | $2.27 \times 10^{-5}$ | $2.57 \times 10^{-7}$ | −6.590 |

METHYL METHACRYLATE POLYMERIZATION

| $T$, °C. | $K^2$ | $R_p$, thermal | $R_i'$[Cat] | log $R_i'/2$ [Cat] |
|---|---|---|---|---|
| 70 | $4.48 \times 10^{-10}$ | $5.92 \times 10^{-6}$ | $1.97 \times 10^{-8}$ | −7.705 |
| 98 | $4.80 \times 10^{-8}$ | $3.02 \times 10^{-5}$ | $7.87 \times 10^{-7}$ | −6.104 |

At 80° Haward and Simpson[15] list a value for "*k*" ($K^2/[M]^2$ in our notation) of $1.91 \times 10^{-8}$. This is in good agreement with our calculated value of $K^2/[M]^2$ equal to $1.84 \times 10^{-8}$. Our thermal rates at 60 and 80° are also in excellent agreement with their reported values of $2.11 \times 10^{-6}$ and $1.09 \times 10^{-5}$, respectively. When our thermal rates are

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[13] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

[14] F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

[15] R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951).

[16] A. V. Tobolsky and J. A. Offenbach, *J. Polymer Sci.*, **16**, 311 (1955).

[17] G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

plotted on a semilogarithmic basis, an activation energy of 19.1 kcal. is obtained. On the basis of some older data,[18,19] Flory has calculated an activation energy of 21 kcal.[20] A compilation by Boundy and Boyer[21] from more recently obtained data, however, indicates an activation energy of 19.2 kcal. and agrees with our result.

For a first-order decomposition, our calculated values of $R_i'/2[\text{Cat}]$ can also be expressed as $k_d f(1 + x)$, in which $k_d$ is the specific first-order rate constant, and $f$ is an efficiency factor. The quantity $x$ is as previously defined. The parameter $f$ expresses the fraction of radicals produced which are capable of initiating polymer chains. Since the accepted mechanism for the decomposition of di-*t*-butyl peroxide involves only radical formation in the primary cleavage,[3-8] then it is sufficient to follow the reaction by means of radical scavengers alone. Comparison of an independent determination of the quantity $k_d$ with $R_i'/2[\text{Cat}]$ should then yield an estimate of the quantity $f(1 + x)$, designated as $f'$. This was achieved by an independent determination of $k_d$ for DTBP in benzene, measuring the disappearance of color of the radical scavenger 2,2-diphenyl-1-picrylhydrazyl.[22]

The rates of disappearance of DPPH, $R_{\text{DPPH}}$ were determined at 70° and computed from the slopes of linear plots of optical density *vs.* time, using a previous calibration of optical density as a linear function of concentration. Four runs were made covering a range in catalyst concentration from 0.279 to 0.511 mole/l. Although there appears to be a slight trend of decreasing values of $R_{\text{DPPH}}/2[\text{Cat}]$ with increasing catalyst concentration, there is only an average deviation of 5% from the mean value of the four runs, $1.44 \times 10^{-8}$. Noting that the exact coincidence with the magnitude of $R_i'/2[\text{Cat}]$ for styrene at 70° is fortuitous, it certainly appears that the factor $f(1 + x)$ is close to unity. Since $f(1 + x)$ has been shown to be nearly temperature independent in initiators for which data were available,[10] it was not considered necessary to repeat these determinations at other temperatures.

## Discussion

Recent radioactive and group determinations have been carried out to ascertain the fraction of termination of radical chains occurring by disproportionation.[23,34] The data for styrene at 25 and 60° shows that termination by combination occurs almost exclusively; hence $x = 0$. From the result quoted above for $f(1 + x)$, it would seem that the true efficiency is very close to unity in styrene, and there is little or no recombination of initiator radicals. At 60° in methyl methacrylate, however, the recent end group determinations indicate a termination reaction occurring mostly by disproportionation. From the ratio $k_{td}/k_{tc}$ tabulated by these workers, a value of 0.85 for $x$ is calculated. The present authors feel that further work should be done in this field before this value of $x$ is regarded as established. The difficulty that arises from using this value of $x$ is that the efficiencies of various initiators in methyl methacrylate all turn out to be lower than in styrene by a factor of approximately two. Perhaps the difficulty in establishing the true value of $x$ lies in the accuracy of the molecular weight determinations.

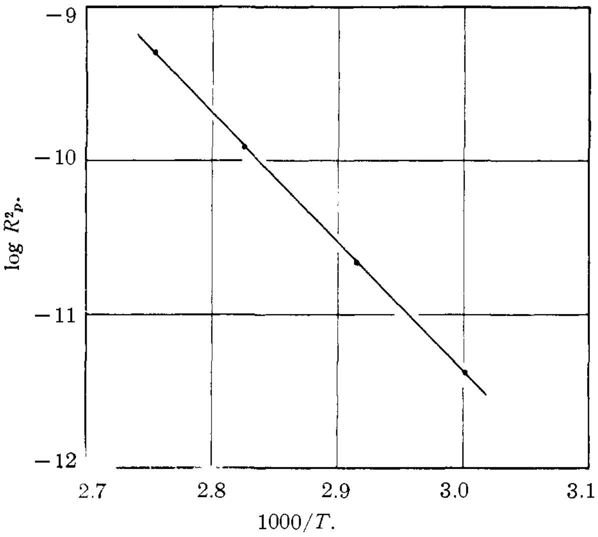

Fig. 3.—Thermal polymerization of styrene.

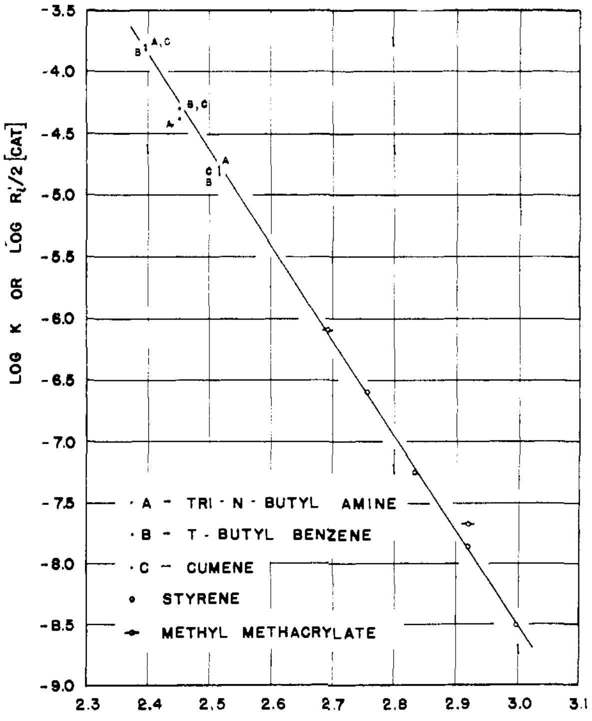

Fig. 4.—Decomposition of DTBP in solution.

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[18] H. Suess, K. Pilch and H. Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937).

[19] G. V. Schulz and E. Huseman, *ibid.*, **B36**, 184 (1937).

[20] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 132.

[21] R. H. Boundy and R. F. Boyer, "Styrene, Its Polymers, Copolymers, and Derivatives," Reinhold Publ. Corp., New York, N. Y., 1952, p. 221.

[22] M. S. Matheson, *et al.*, This Journal, **73**, 1700 (1951).

[23] J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Polymer Sci.*, **12**, 449 (1954).

[24] J. C. Bevington, H. W. Melville and R. P. Taylor, *ibid.*, **14**, 463 (1954).

A plot log $R_i'/2[\text{Cat}]$ *vs.* $1/T$ is presented in Fig. 3. On this same scale are also shown data obtained for $k_d$ by Raley, Rust and Vaughan[8] at higher temperatures in three different solvents. A very satisfactory correlation exists between the two sets of data, and the equation which gives the best fit to all the data in solution is

$$R_i'/2[\text{Cat}] = k_d = 2.8 \times 10^{14} \exp(-35.0 \text{ kcal.}/RT) \quad (4)$$

The excellent agreement between the data of Raley, Rust and Vaughan with our results for styrene, taken in conjunction with the unity value obtained for $f(1 + x)$ in styrene indicate the equivalence of $R_i'/2[\text{Cat}]$ with $k_d$ in solution. With methyl methacrylate, the situation is not so clean cut for the reasons outlined above.

Figure 4 presents a composite of all results obtained both in the gas phase and in solution. The solution values of Raley, Rust and Vaughan are shown as an average of the values for *t*-butyl benzene and cumene. The line drawn through the gas phase points is that of Lossing and Tickner.[6] If this line be accepted as correct, then our values would be substantially above the gas phase values, extrapolated to our working temperatures, by a factor of three. Since all solution points lie on the same line, however, a more direct comparison can be made between the solution data of Raley, Rust and Vaughan at higher temperatures and the gas phase line. Here the discrepancy is only a factor of 1.6. This divergence is, of course, caused by the lower activation energy which we found, of 35.0 kcal., as compared with the over-all activation energy in the gas phase, which has been cited by Lossing and Tickner as 38 kcal. The difference of 3.0 kcal. appears to be within the range of variation of activation energy obtained in the gas phase by different investigators, although we consider our values to be correct within 1.0 kcal. If more weight be placed on Szwarc's data in drawing the gas phase line, then the divergence is not nearly so great. On the basis of theoretical considerations[25] a cage recombination of primary radicals in solution might be expected to reverse the discrepancy, and cause higher rates in the gas phase, instead of in solution.

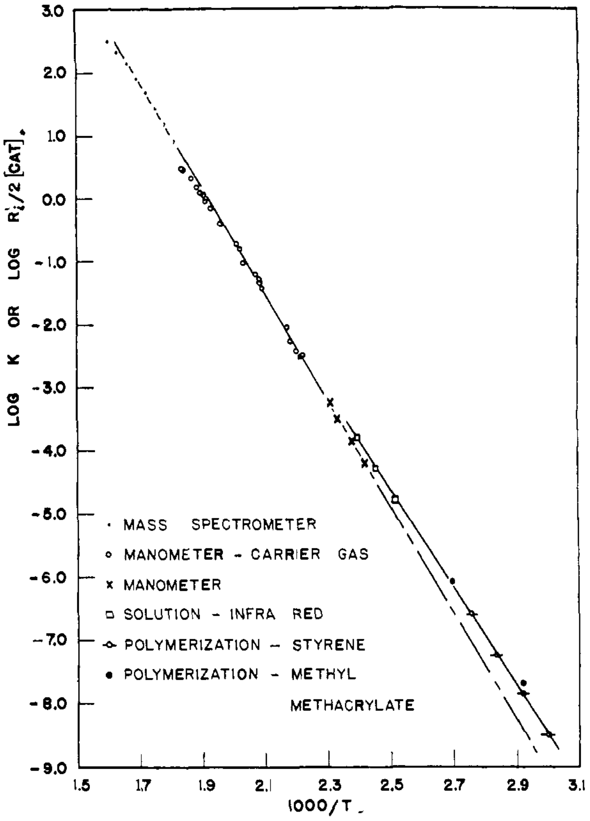

Fig. 5.—Decomposition of di-*t*-butyl peroxide.

A recent series of studies of Szwarc and coworkers has been published on the decomposition rates of diacetyl peroxide in various solvents as well as in the gas phase.[26-28] In contrast to our results with DTBP, higher activation energies and lower rate constants were found in solutions, although both media showed a first-order decomposition.

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[25] J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[26] A. Rembaum and M. Szwarc, THIS JOURNAL, **76**, 5975 (1954).

[27] M. Levy, M. Steinberg and M. Szwarc, *ibid.*, **76**, 5978 (1954).

[28] M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BOSTON UNIVERSITY]

# Light Scattering Studies of Poly-soap Solutions[1]

BY SISIR K. SINHA AND A. I. MEDALIA[2] with the technical assistance of DOROTHY P. HARRINGTON

RECEIVED APRIL 23, 1956

A new type of poly-soap is described. This is a copolymer of styrene with potassium styrylundecanoate, and thus contains base units with terminal carboxylate groups. Dye solubilization data and solubility behavior of the poly-soap and poly-acid are reported. Light scattering measurements have been made of poly-soaps prepared from poly-acids of known molecular weight. In pure aqueous solution, the apparent molecular weight of the poly-soaps was found to be from one-fifth to one-half of the actual molecular weight. In the presence of added electrolyte (KCl, 0.01–0.1 *N*), values fairly close to the actual molecular weights were obtained. In more concentrated salt solutions, the poly-soap showed evidence of aggregation.

Soaps are known to form aggregates, called micelles, in aqueous solution above a certain concentration (the critical micelle concentration, or c.m.c.). Despite extensive study,[3] there remains considerable disagreement at present concerning the size of the micelle and its dependence on con-

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[1] Presented at 128th National Meeting of American Chemical Society, Minneapolis, Sept. 15, 1955.

[2] Godfrey L. Cabot, Inc., Research and Development Department, Cambridge, Massachusetts.

[3] M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, New York, N. Y., 1955.