[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ROHM AND HAAS COMPANY]

Chain Transfer in the Polymerization of Methyl Methacrylate. I. Transfer with Monomer and Thiols. The Mechanism of the Termination Reaction at 60°[1]

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RECEIVED APRIL 22, 1955

The initial rate (R_p) and number average degree of polymerization ($\bar{P}_n$) of methyl methacrylate at 60° with the initiator 2,2'-azobis-(isobutyronitrile) (AIN) have been determined. $\bar{P}_n$ values for the unfractionated low-conversion polymers were obtained from intrinsic viscosities in benzene by the equation $\bar{P}_n = 2.22 \times 10^3 [\eta]^{\frac{1}{0.76}}$ of Schuele, Kinsinger and Fox. The data yield the relations $R_p = 3.04 \times 10^{-3} (\text{AIN})^{1/2}$ moles l.$^{-1}$ sec.$^{-1}$ and $1/\bar{P}_n = 2.97 \times 10^{-3} (\text{AIN})^{1/2} + 0.7 \times 10^{-5}$. The monomer transfer constant is thus 0.7×10^{-5}, in good agreement with the value reported by Baysal and Tobolsky. Taking 8.8×10^{-6} sec.$^{-1}$ as the decomposition rate constant of AIN, the present results are compatible with an initiator efficiency of about 50% and a termination reaction which is predominantly disproportionation. On this basis, new values are suggested for the propagation and termination rate constants at 60°. Chain transfer constants for two aromatic and five aliphatic thiols were determined from $\bar{P}_n$ measurements. The greater transfer activity of the aromatic thiols is attributed to a resonance stabilization of the corresponding sulfenyl radicals. Electron-withdrawing substituents have little or no effect on the transfer activity of primary aliphatic thiols. Substitution of methyl groups on the α-carbon atom of the thiol leads to decreasing transfer activity, probably because of increased steric hindrance.

Introduction

The kinetics of the free radical initiated polymerization of methyl methacrylate has been studied by several investigators. Schulz and co-workers[2,3] determined the rate and degree of polymerization at 50 and 70° with the initiator benzoyl peroxide. Their data were combined with radical lifetime measurements by Matheson, Auer, Bevilacqua and Hart[4] to obtain values of the rate constants for the propagation, termination and monomer transfer reactions. Arnett[5] has studied the polymerization at 50 and 77° with the initiator 2,2'-azobis-(isobutyronitrile). A limited amount of data at 60° with the same initiator is given by Bonsall, Valentine and Melville.[6] Baysal and Tobolsky[7] studied the polymerization at 60° with various initiators, including benzoyl peroxide and 2,2'-azobis-(isobutyronitrile). However, some aspects of the polyization mechanism remain uncertain.

A rather wide range of values has been reported for the monomer transfer constant, *i.e.*, 1.0×10^{-5} at 60°,[7] 3.8×10^{-5} at 50°,[5a] 5.5×10^{-5} at 60°,[6] and 6.25×10^{-5} at 60°.[4] These values may be compared with the single value 6.0×10^{-5} at 60° reported for the monomer styrene.[8] It has often been concluded that the termination reaction in methyl methacrylate polymerization occurs by the *combination* of two polymer radicals to form a single polymer molecule.[4,5,7] However, examination of the kinetic evidence leads one to question the validity of this conclusion. As will be shown, the mechanism of termination is intimately bound to the initiator efficiency. Determination of these parameters requires accurate measurement of the number average degree of polymerization. The present investigation, employing the initiator 2,2'-azobis-(isobutyronitrile) at 60°, was undertaken with the view of gaining further information on the monomer transfer and termination reactions.

The series of papers by Mayo and co-workers[9] on the monomer styrene provides an excellent guide for the interpretation of chain transfer measurements.[10] In particular, Gregg, Alderman and Mayo[11] determined the transfer constants of four thiols with styrene at 60 and 100° and concluded that α-methyl group substitution decreases while α-carbethoxy substitution increases the reactivity of a thiol toward polystyrene radicals. The only reported values for the transfer constant of thiols with methyl methacrylate are 0.8 (40–100°) for 1-pentanethiol[12] and 0.67 ± 0.03 (60°) for 1-butanethiol.[13] The present investigation provides transfer constants for two aromatic and five aliphatic thiols, thus permitting an evaluation of the influence of thiol structure on reactivity toward poly-(methyl methacrylate) radicals.

Theoretical

The Mechanism of Free Radical Polymerization.—The following kinetic scheme is similar to those employed by previous investigators

$$\begin{array}{llll} & & \text{Rate} & \\ \text{Initiation:} & \text{I} \xrightarrow{k_d} 2f\text{R}\cdot & 2k_d f(\text{I}) & (1) \\ \text{Propagation:} & \text{R}\cdot + \text{M} \xrightarrow{k_p} \text{R}\cdot & k_p(\text{M})(\text{R}\cdot) & (2) \\ \text{Monomer transfer:} & \text{R}\cdot + \text{M} \xrightarrow{k_m} \text{P} + \text{M}\cdot & k_m(\text{M})(\text{R}\cdot) & (3) \\ \text{Thiol transfer:} & \text{R}\cdot + \text{S} \xrightarrow{k_s} \text{P} + \text{S}\cdot & k_s(\text{S})(\text{R}\cdot) & (4) \end{array}$$

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[1] Presented in part at the Fifth Miniature Meeting of the Philadelphia Section, January, 1953 (Abstracts, p. 73) and at the 123rd Meeting of the American Chemical Society, Los Angeles, March, 1953 (Abstracts, p. 5Q).

[2] G. V. Schulz and F. Blaschke, *Z. physik. Chem.*, **51B**, 75 (1942).

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

[4] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

[5] (a) L. M Arnett, *ibid.*, **74**, 2027 (1952); (b) L. M. Arnett and J. H. Peterson, *ibid.*, **74**, 2031 (1952).

[6] E. P. Bonsall, L. Valentine and H. W. Melville, *Trans. Faraday Soc.*, **48**, 763 (1952).

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

[8] (a) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951); (b) D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

[9] R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953), and previous papers there listed.

[10] Similar experiments on the polymerization of methyl methacrylate in various solvents have been described (S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc.* (*London*), **A202**, 485 (1950); *ibid.*, **A214**, 247 (1952)). Our own investigation of the kinetics of the solution polymerization of methyl methacrylate will be reported by J. L. O'Brien, J. R. Panchak and T. G. Fox.

[11] R. A. Gregg, D. M. Alderman and F. R. Mayo, THIS JOURNAL, **70**, 3740 (1948).

[12] W. V. Smith, *ibid.*, **68**, 2059 (1946).

[13] C. Walling, *ibid.*, **70**, 2561 (1948).

$$\text{Combination:} \qquad \mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_{\mathrm{tc}}} \mathrm{P} \qquad 2k_{\mathrm{tc}}(\mathrm{R}\cdot)^2 \quad (5)$$

$$\text{Disproportionation:} \quad \mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_{\mathrm{td}}} \mathrm{P} + \mathrm{P} \quad 2k_{\mathrm{td}}(\mathrm{R}\cdot)^2 \quad (6)$$

where I is the initiator, M is the monomer and S is the thiol; R· is an active polymer radical, M· and S· are free radicals derived from the monomer and thiol, respectively; P is a polymer molecule; the k's are the rate constants for the various reactions, *e.g.*, k_{d} is the rate constant for the first-order decomposition of the initiator, and f is an efficiency factor for the conversion of initiator radicals to active polymer radicals (initiator efficiency). The steady state condition is expressed by the relation

$$2k_{\mathrm{d}}f(\mathrm{I}) = 2k_{\mathrm{tc}}(\mathrm{R}\cdot)^2 + 2k_{\mathrm{td}}(\mathrm{R}\cdot)^2 \qquad (7)$$

from which

$$(\mathrm{R}\cdot) = \left[\frac{k_{\mathrm{d}}f(\mathrm{I})}{k_{\mathrm{tc}} + k_{\mathrm{td}}}\right]^{1/2} \qquad (8)$$

Equation for the Rate of Polymerization.—The over-all rate (R_{p}) may be taken equal to the rate of the propagation reaction. Hence

$$R_{\mathrm{p}} = \frac{-\mathrm{d}(\mathrm{M})}{\mathrm{d}t} = k_{\mathrm{p}}[k_{\mathrm{d}}f/(k_{\mathrm{tc}} + k_{\mathrm{td}})]^{1/2}(\mathrm{M})(\mathrm{I})^{1/2} \qquad (9)$$

Equation 9 shows that the rate of polymerization should be proportional to the square root of the initiator concentration.

Equation for the Degree of Polymerization.—The number average degree of polymerization ($\bar{P}_{\mathrm{n}}$) is equal to the rate of polymerization of monomer units divided by the total rate of formation of polymer molecules,[14] *i.e.*

$$\bar{P}_{\mathrm{n}} = \frac{k_{\mathrm{p}}(\mathrm{M})(\mathrm{R}\cdot)}{k_{\mathrm{tc}}(\mathrm{R}\cdot)^2 + 2k_{\mathrm{td}}(\mathrm{R}\cdot)^2 + k_{\mathrm{m}}(\mathrm{M})(\mathrm{R}\cdot) + k_{\mathrm{s}}(\mathrm{S})(\mathrm{R}\cdot)} \qquad (10)$$

From equations 8 and 10, we obtain

$$\frac{1}{\bar{P}_{\mathrm{n}}} = \frac{(k_{\mathrm{d}}f)^{1/2}}{k_{\mathrm{p}}}\left[\frac{k_{\mathrm{tc}} + 2k_{\mathrm{td}}}{(k_{\mathrm{tc}} + k_{\mathrm{td}})^{1/2}}\right]\frac{(\mathrm{I})^{1/2}}{(\mathrm{M})} + \frac{k_{\mathrm{m}}}{k_{\mathrm{p}}} + \frac{k_{\mathrm{s}}}{k_{\mathrm{p}}}\frac{(\mathrm{S})}{(\mathrm{M})} \qquad (11)$$

By definition, $C_{\mathrm{m}} = k_{\mathrm{m}}/k_{\mathrm{p}}$ and $C_{\mathrm{s}} = k_{\mathrm{s}}/k_{\mathrm{p}}$, where C_{m} is the monomer transfer constant and C_{s} is the transfer constant of the thiol. According to equation 11, there is a linear relation between the reciprocal degree of polymerization (in the absence of thiol) and the square root of the initiator concentration. Conversely, there should be a linear relation between the reciprocal degree of polymerization at constant initiator concentration and the thiol–monomer ratio. The transfer constant of the thiol is given by the slope of this line.

Validity of Assumptions.—Implicit in the above kinetic treatment are the following assumptions.

(a) *The rate of thermal polymerization at 60° is negligible in comparison with the initiated rates.* As will be seen, the published data[6,15] supporting this conclusion are confirmed in our own experiments.

(b) *The monomer concentration remains constant at its actual value at 60°, which is 8.96 moles per liter.* The concentration of methyl methacrylate in the very dilute solutions of the thiols does not differ significantly from this figure. Except where specifically stated, no polymerizations were carried beyond 5–8% conversion. The initial rate of polymerization is exactly constant in this range.[6]

(c) *Chain transfer with the initiator 2,2′-azobis-(isobutyronitrile) is negligible.*[7]

(d) *Chain transfer with thiols has no effect on the rate of polymerization.* Within the limits of experimental error, this condition holds true for all of the aliphatic thiols. With the aromatic thiols, however, a slight retardation was observed. The relative polymerization rates at the highest concentrations of benzenethiol and 2-naphthalenethiol were 0.84 and 0.77, respectively. Under such conditions, the apparent chain transfer constants calculated from equation 11 will be slightly greater than the true values.[16]

Experimental

Purification of Materials.—Methyl methacrylate (MMA) was purified in the manner previously described.[17] The fraction boiling at 46.0° (100 mm.) had $n^{25}\mathrm{D}$ 1.4120, $d^{30}{}_4$ 0.9311 and $d^{60}{}_4$ 0.8968. 2,2′-Azobis-(isobutyronitrile) (AIN) was recrystallized three times from benzene, m.p. 103.0–103.5° dec. on the Fisher–Johns apparatus. The liquid thiols were fractionally distilled under nitrogen; 2-naphthalenethiol was recrystallized from ethanol. In most cases, the purity of the thiols was established by iodometric analysis.

Preparation of Samples.—Pyrex ampoules, 200 × 18 mm., were cleaned with acid dichromate solution and then allowed to stand overnight with dilute aqueous sulfurous acid. After repeated rinsing with distilled water, they were dried in an oven at 80° and then flamed on the high vacuum line immediately before use. About 10 g. of a solution containing the desired amounts of MMA, AIN and thiol was weighed into an ampoule. The latter was immersed in liquid nitrogen and evacuated to less than 10^{-5} mm. The ampoule was then isolated from the system and allowed to warm sufficiently to melt the contents. The liquid was refrozen in liquid nitrogen and the degassing operation repeated. Finally, the ampoules were sealed at less than 10^{-5} mm.

Polymerization.—The sealed ampoules were allowed to warm to room temperature, when they were shaken vigorously and immersed in an oil-bath held at 60.0 ± 0.1° by a mercury thermoregulator. After the proper reaction time (calculated to give about 5% conversion), the ampoules were removed from the bath and immediately frozen in liquid nitrogen.

Isolation of Polymer.—The frozen ampoules were opened and the contents, after thawing, were washed into large beakers with about 30 ml. of acetone containing a little hydroquinone. About ten volumes of a mixture of 90% methanol and 10% water was then added with rapid stirring. The precipitated polymer was collected on a tared sintered-glass filter and washed thoroughly with the precipitant mixture. After drying at room temperature in a vacuum desiccator for several hours, the samples were heated in a vacuum oven at 60° for at least 16 hours.

Determination of Intrinsic Viscosity.—Measurements were made at 30.00 ± 0.01° on filtered solutions of polymer in freshly distilled benzene. Two Ubbelohde viscometers, having efflux times of 69.70 ± 0.05 and 71.70 ± 0.05 seconds for the pure solvent, were employed. These viscometers had previously been calibrated for the kinetic energy correction, which was applied to all the data. Values of η_{sp} in the range of 0.2–0.5 were used to calculate intrinsic viscosity from the relation

$$[\eta] = \ln \eta_{\mathrm{r}}/c + {}^1/_4[\eta_{\mathrm{sp}}/c - \ln \eta_{\mathrm{r}}/c] \qquad (12)$$

which is derived from the familiar Huggins equation,[18] by taking the parameter k equal to ${}^3/_8$, a condition which holds for solutions of poly(MMA) in benzene.[19] The intrinsic

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(14) Note that the coefficient 2 has been dropped from the expression for the rate of termination by combination (equation 5), because in this instance the rate of formation of polymer molecules is one-half the rate of disappearance of polymer radicals.

(15) C. Walling and E. R. Briggs, THIS JOURNAL, **68**, 1141 (1946).

(16) W. H. Stockmayer, R. O. Howard and J. T. Clarke, *ibid.* **75**, 1756 (1953).

(17) S. Loshaek and T. G. Fox, *ibid.*, **75**, 3544 (1953).

(18) M. L. Huggins, *ibid.*, **64**, 2716 (1942).

(19) T. G. Fox, unpublished results.

viscosity values reported in this paper are in the customary units of deciliters/gram.

Determination of Residual Thiol.[20]—In this instance only, polymerizations were allowed to proceed to conversions as high as 80%. A portion of the sample was then analyzed for residual thiol by amperometric titration with 0.025 *N* silver nitrate.[21] The solvent was a mixture of ethanol and acetone, the latter being added to dissolve the polymer. A second portion of the sample was diluted with the original monomer solution to a polymer content of less than 12%. The precise polymer content was then determined by means of a differential refractometer, which had previously been calibrated with known polymer solutions.[15] From these measurements, the consumptions of monomer and thiol were easily calculated.

Results

Rate of Polymerization of MMA with AIN at 60°.—The rate of polymerization R_p was determined gravimetrically in fifteen experiments, with AIN concentrations from 4.28×10^{-4} to 61.5×10^{-4} mole liter^{-1}, by means of the equation

$$R_p = 2.49 \times 10^{-5} (d\alpha/dt) \qquad (13)$$

where R_p is the rate in moles liter^{-1} sec.$^{-1}$ and $d\alpha/dt$ is the observed rate of conversion in per cent. per hour. The data are given in Table I.

As predicted by equation 9, a plot of R_p against $(AIN)^{1/2}$ gave a straight line passing through the origin (Fig. 1). The slope of this line was found to be 3.04×10^{-3}, corresponding to the relation

$$R_p = 3.04 \times 10^{-3} (AIN)^{1/2} (\text{moles l.}^{-1} \text{sec.}^{-1}) \qquad (14)$$

TABLE I

RATE OF POLYMERIZATION OF METHYL METHACRYLATE WITH 2,2'-AZOBIS-(ISOBUTYRONITRILE) AT 60°

(AIN) × 10^4, moles/l.	$d\alpha/dt$, %/hr.	$R_p \times 10^5$, moles/l. sec.	$R_p/(AIN)^{1/2}$ (× 10^3)
4.28	2.45	6.10	2.95
4.28	2.48	6.18	2.98
9.12	3.73	9.29	3.08
9.12	3.73	9.29	3.08
16.3	4.97	12.4	3.07
16.3	5.08	12.6	3.12
24.2	6.24	15.5	3.15
25.7	6.32	15.7	3.10
31.8	6.67	16.6	2.94
31.8	6.89	17.2	3.05
32.7	7.13	17.8	3.10
33.9	6.91	17.2	2.96
33.9	6.98	17.4	2.99
46.6	8.08	20.1	2.95
61.5	9.83	24.5	3.12

The data of Baysal and Tobolsky[7] (six gravimetric experiments) yield the relation $R_p = 2.93 \times 10^{-3} (AIN)^{1/2}$, while those of Bonsall, Valentine and Melville[6] (three dilatometric experiments) correspond to $R_p = 3.11 \times 10^{-3} (AIN)^{1/2}$. The agreement among the three sets of results is rather good for this type of kinetic measurement.[22]

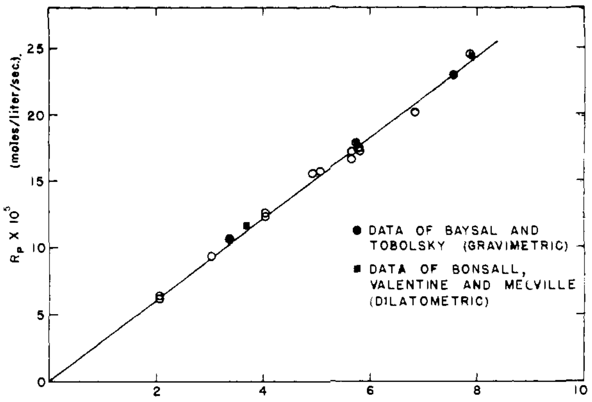

Fig. 1.—Rate of polymerization of methyl methacrylate with 2,2'-azobis-(isobutyronitrile) at 60° and a comparison with previous work (the line is based only on the results obtained in the present investigation).

Degree of Polymerization of MMA with AIN at 60°.—The number average degree of polymerization was determined from intrinsic viscosity in twenty-two experiments, with (AIN) in the range 4.28–79.6 × 10^{-4} mole l.$^{-1}$ by means of the equation

$$\bar{P}_n = 2.22 \times 10^3 [\eta]_{C_6H_6}^{\frac{1}{0.76}} \qquad (15)$$

of Schuele, Kinsinger and Fox.[23] Previous relations developed by Baxendale, Bywater and Evans[24] and by Baysal and Tobolsky[7] for unfractionated low-conversion poly (MMA) yield somewhat higher values for $\bar{P}_n$. As discussed elsewhere,[23] it appears that equation 15 is the most accurate re-

TABLE II

DEGREE OF POLYMERIZATION OF METHYL METHACRYLATE AT 60°

(AIN) × 10^4, moles/l.	$[\eta]C_6H_6$, dl. g.$^{-1}$	$1/\bar{P}_n$ (× 10^5)	$\frac{1/\bar{P}_n - C_m}{(AIN)^{1/2}}$ (× 10^3)
4.28	4.02	7.20	3.13
4.28	4.00	7.25	3.15
9.12	3.20	9.73	2.98
9.12	3.18	9.80	3.01
9.61	3.15	9.93	2.97
16.3	2.65	12.46	2.90
16.3	2.59	12.83	3.00
25.7	2.30	15.03	2.82
25.7	2.27	15.29	2.87
31.8	2.04	17.60	2.99
31.8	2.03	17.70	3.01
33.9	1.96	18.54	3.06
33.9	1.93	18.92	3.13
35.3	1.97	18.43	2.98
35.5	2.04	17.60	2.83
41.6	1.94	18.81	2.80
43.2	1.88	19.58	2.87
47.7	1.75	21.52	3.01
47.7	1.71	22.21	3.11
66.3	1.57	24.83	2.96
79.6	1.46	27.32	2.98
79.6	1.45	27.64	3.02

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(20) Miss E. Cohn and Mrs. J. Haug assisted in these experiments.

(21) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

(22) Our own dilatometric experiments have indicated a rate equation practically identical to that of Bonsall, Valentine and Melville,[7] suggesting that the gravimetric rate results may be slightly low. Perhaps the explanation lies in mechanical losses during the isolation of the polymer. In any event, the differences are so small that they have no significant effect on the interpretations given in the present paper.

(23) E. M. Schuele, J. Kinsinger and T. G. Fox, to be published.

(24) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).

lationship yet available.[25] The data are given in Table II.

As predicted by equation 11, a plot of $1/\bar{P}_n$ against $(\mathrm{AIN})^{1/2}$ gave a straight line with a positive intercept (Fig. 2). By a least squares method, the equation corresponding to this line was found to be

$$\frac{1}{\bar{P}_n} = 2.97 \times 10^{-3}(\mathrm{AIN})^{1/2} + 0.7 \times 10^{-5} \quad (16)$$

The intercept gives the value 0.7×10^{-5} for C_m, the monomer transfer constant. The data of Baysal and Tobolsky[7] yield the relation $1/\bar{P}_n = 2.43 \times 10^{-3}(\mathrm{AIN})^{1/2} + 1.0 \times 10^{-5}$, in good agreement with our value of C_m. In a limited investigation of this subject, Bonsall, Valentine and Melville[6] obtained the relation $1/\bar{P}_n = 1.77 \times 10^{-3}(\mathrm{AIN})^{1/2} + 5.5 \times 10^{-5}$, corresponding to a higher value of C_m. However, the three molecular weight determinations reported in their paper do not appear sufficient for an accurate evaluation of this constant.

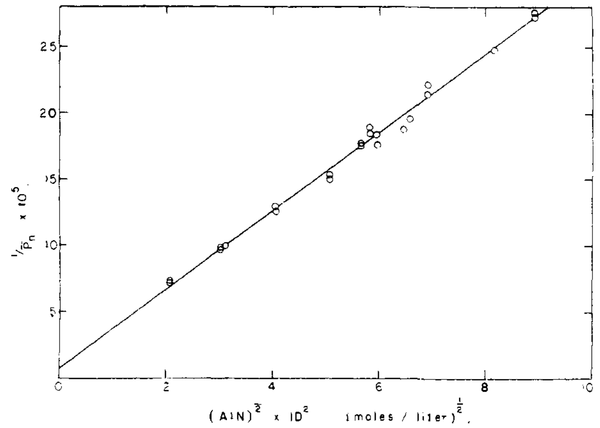

Fig. 2.—Reciprocal number average degree of polymerization of methyl methacrylate with 2,2′-azobis-(isobutyronitrile) at 60°.

Degree of Polymerization of MMA in the Presence of Thiols.—In these experiments, polymerizations were carried out in which the concentration of AIN was maintained constant while the thiol–monomer ratio was progressively increased. Two or three such series at AIN concentrations from 25×10^{-4} to 100×10^{-4} mole liter^{-1} were made with each thiol. The number average degrees of polymerization were calculated from intrinsic viscosity by means of equation 15, which was shown to apply both to polymers prepared with and without transfer agent.[23] The data are given in Table III.

In the last column of Table III are listed the values of C_s given by the slope of a plot of $1/\bar{P}_n$ against S/M. As predicted by equation 11, linear plots were observed (Fig. 3). Except in the case of 2-naphthalenethiol, these lines extrapolated to the theoretical $1/\bar{P}_n$ value (at zero thiol concentration) calculated from equation 16. The failure of this extrapolation with 2-naphthalenethiol may be related to the fact that this thiol produced a significant amount of retardation. In any event, the values of the transfer constant given for this thiol are probably a little high.[16]

TABLE III

DEGREE OF POLYMERIZATION OF MMA IN THE PRESENCE OF THIOLS

AIN ($\times 10^4$) moles/l.	S/M ($\times 10^4$)	$[\eta]C_6H_6$	$(1/\bar{P}_n)$ ($\times 10^5$)	C_s
		Benzenethiol		
64.7	1.00	0.86	5.48	2.7
64.7	2.95	.49	11.49	
64.7	7.14	.31	20.98	
100	2.78	.50	11.19	2.7
100	7.07	.30	21.92	
		2-Naphthalenethiol		
36.6	0.98	0.70	7.18	3.4
36.6	2.01	.50	11.19	
36.6	3.03	.42	14.07	
99.8	1.31	.57	9.42	2.7
99.8	2.56	.43	13.64	
99.8	5.01	.32	20.13	
		1-Butanethiol		
25.0	4.04	1.00	4.49	0.67
25.0	5.99	.83	5.75	
25.0	8.97	.66	7.78	
41.6	3.83	.93	4.95	0.63
41.6	7.87	.68	7.46	
41.6	13.7	.50	11.19	
99.0	4.99	.78	6.24	0.68
99.0	10.0	.57	9.42	
99.0	14.7	.45	12.85	
		Ethyl mercaptoacetate		
35.6	1.05	1.64	2.34	0.64
35.6	2.00	1.37	2.97	
35.6	4.01	1.06	4.16	
35.6	8.17	0.70	7.18	
35.6	12.2	0.55	9.87	
99.8	6.77	0.66	7.78	0.61
99.8	19.2	0.40	15.01	
		2-Mercaptoethanol		
4.28	0.59	3.34	0.92	0.61
4.28	1.84	1.98	1.83	
4.28	4.18	1.24	3.39	
4.28	5.30	1.14	3.78	
49.0	2.87	1.06	4.16	0.63
49.0	5.97	0.81	5.93	
49.0	12.8	0.54	10.11	
100	3.60	0.85	5.56	0.62
100	5.40	0.74	6.68	
100	7.39	0.65	7.92	
		2-Propanethiol		
25.2	3.03	1.46	2.73	0.39
25.2	6.10	1.10	3.97	
25.2	12.2	0.77	6.34	
25.2	17.9	0.62	8.42	
99.4	6.40	0.85	5.56	0.37
99.4	12.3	0.67	7.61	
99.4	18.5	0.25	27.86	
		2-Methyl-2-propanethiol		
39.2	3.71	1.52	2.59	0.17
39.2	9.02	1.19	3.58	
39.2	17.0	0.96	4.74	
100	3.39	1.22	3.46	0.19
100	11.2	0.93	4.95	
100	18.7	0.76	6.45	

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(25) If this conclusion is correct, transfer constants with methyl methacrylate previously reported are too low by a factor of about 1.2.

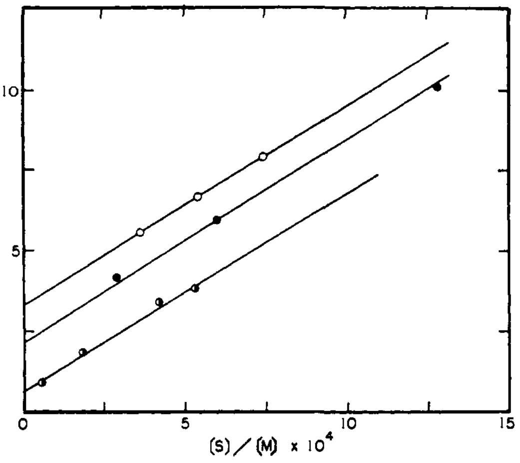


Fig. 3.—Chain transfer of methyl methacrylate with 2-mercaptoethanol at 60°.

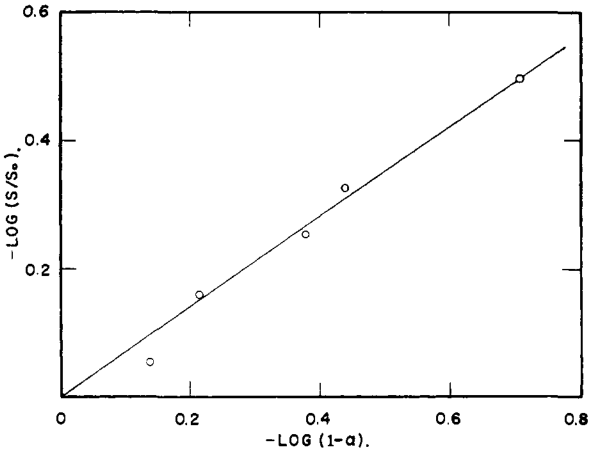


Fig. 4.—Relative rates of consumption of methyl methacrylate and 1-butanethiol at 60°.

Relative Rates of Consumption of MMA and 1-Butanethiol.—We were interested to determine the transfer constant of one of the thiols by a method independent of molecular weight measurements. A method which has been described for the monomer styrene[11] involves the determination of the rates of consumption of monomer and thiol. These are related to the transfer constant C_s by the equation

$$\log (S/S_0) = C_s \log (1 - \alpha) \qquad (17)$$

whers S_0 is the initial concentration of thiol and S is the concentration of thiol which remains after the fractional conversion α of monomer to polymer. Some data for the system MMA:1-butanethiol are given in Table IV.

TABLE IV

RATES OF CONSUMPTION OF MMA AND 1-BUTANETHIOL

α	S/S_0	$-\log (S/S)_0$	$-\log (1 - \alpha)$
0.273	0.886	0.053	0.139
.389	.692	.160	.214
.581	.559	.253	.378
.637	.473	.325	.440
.805	.320	.495	.710

As predicted by equation 17, a plot of log (S/S_0) against log $(1 - \alpha)$ gave a straight line passing through the origin (Fig. 4). The slope of 0.70 is in satisfactory agreement with the average (0.66) of the values of C_s given for 1-butanethiol in Table III. By a radioactive tracer method, Walling[13] obtained a C_s value of 0.67 ± 0.03 at 60°. The agreement in the transfer constants of 1-butanethiol given by the three methods confirms the accuracy of equation 15.

Discussion

The Efficiency of Initiation and the Mechanism of Termination.—Comparison of the theoretical rate equation 9 with the observed relation 14 shows that

$$k_p[k_d f/(k_{tc} + k_{td})]^{1/2}(M) = 3.04 \times 10^{-3} \qquad (18)$$

Similarly, equations 11 and 16 for the reciprocal degree of polymerization yield

$$\frac{(k_d f)^{1/2}}{k_p(M)}\left[\frac{k_{tc} + 2k_{td}}{(k_{tc} + k_{td})^{1/2}}\right] = 2.97 \times 10^{-3} \qquad (19)$$

Multiplication of equations 18 and 19 gives

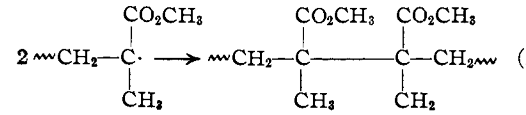
$$k_d f\left(\frac{k_{tc} + 2k_{td}}{k_{tc} + k_{td}}\right) = 9.04 \times 10^{-6} \qquad (20)$$

The rate constant k_d for the first-order decomposition in AIN in methyl isobutyrate solution at 60°,[26] is 8.8×10^{-6} sec.$^{-1}$. If we assume that this initiator decomposes at an identical rate in the structurally similar solvent methyl methacrylate, equation 20 reduces to

$$f\left(\frac{k_{tc} + 2k_{td}}{k_{tc} + k_{td}}\right) = 1.03 \qquad (21)$$

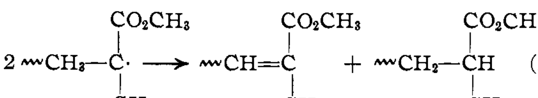
Equation 21 may be satisfied by any one of the following sets of conditions

(a) The termination reaction is exclusively *combination* (equation 22) and the initiator efficiency is 100%.

 (22)

$$2\,\sim\!\!\sim CH_2-\underset{CH_2}{\overset{CO_2CH_3}{C}}\cdot \longrightarrow \sim\!\!\sim CH_2-\underset{CH_3}{\overset{CO_2CH_3}{C}}-\underset{CH_2}{\overset{CO_2CH_3}{C}}-CH_2\sim\!\!\sim \qquad (22)$$

(b) The termination reaction is exclusively *disproportionation* (equation 23) and the initiator efficiency is about 50%.

 (23)

$$2\,\sim\!\!\sim CH_3-\underset{CH_2}{\overset{CO_2CH_3}{C}}\cdot \longrightarrow \sim\!\!\sim CH{=}\underset{CH_3}{\overset{CO_2CH_3}{C}} + \sim\!\!\sim CH_2-\underset{CH_3}{\overset{CO_2CH_3}{CH}} \qquad (23)$$

(c) The termination reaction is composed of both combination and disproportionation, while the initiator efficiency lies somewhere between 50 and 100%.

Now it has been shown that the number average molecular weight–intrinsic viscosity relations are substantially identical for poly(MMA) samples prepared with AIN at 60° either with or without 1-butanethiol as transfer agent. This as well as other evidence from molecular weight studies[23] seems to be consistent only with the conclusion that the termination reaction for MMA at 60° is predomi-

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[26] This value was taken from an Arrhenius plot of data obtained in this Laboratory at 50 and 70° by both gas evolution and polarographic methods (S. Gratch and J. L. Kice, paper presented at the 126th Meeting of the American Chemical Society, New York, September, 1954 (Abstracts, p. 3S).

nantly disproportionation. The same conclusion was reported from studies on the rate of thermal degradation of various poly(MMA) samples prepared at 60°.[27] More direct evidence for the nature of the MMA termination reaction at 60° has appeared recently. Bevington, Melville and Taylor[28] find that poly(MMA) formed at 60° by the action of AIN labeled with C^{14} in the methyl group contains an average of 1.08 initiator fragments per molecule. This indicates that at 60° disproportionation occurs about six times as frequently as combination, or, more precisely, that $k_{td}/k_{tc} = 5.75$. Substitution of this result into equation 21 gives $f = 0.56$, *i.e.*, an initiator efficiency of 56%. The latter is in good agreement with the efficiency of 52% at 50° obtained by Arnett and Peterson[5b] using AIN labeled with C^{14} in the cyano groups.[29] An initiator efficiency in the neighborhood of 50% is not surprising when it is considered that even the most reactive radical scavengers in inert solvents capture the radicals from AIN with an efficiency of only 60–70% at 62.5°.[30]

A Re-evaluation of the Absolute Rate Constants at 60°.[31]—Upon dividing equation 18 by equation 19 and substituting the value (M) = 8.96, we obtain

$$\frac{k_p^2}{k_{tc} + 2k_{td}} = 1.27 \times 10^{-2} \qquad (24)$$

According to the radical lifetime measurements of Matheson, Auer, Bevilacqua and Hart[4]

$$\frac{k_p}{2(k_{tc} + k_{td})} = 2.06 \times 10^{-5} \qquad (25)$$

Solution of the above equations with the aid of the relation[28] $k_{td} = 5.75\, k_{tc}$ gives

$$k_p = 573$$
$$k_{tc} = 0.20 \times 10^7$$
$$k_{td} = 1.19 \times 10^7$$

These values are somewhat different from those originally calculated by Matheson and co-workers[4] using the data of Schulz.[3,32]

Comparison of Some Rate Constants for Monomer Transfer.—The C_m values for MMA, styrene,[8] and vinyl acetate[33] may be combined with the corresponding k_p values[34] to calculate the specific rate constants (k_m) of the monomer transfer reaction. The results are given in Table V.

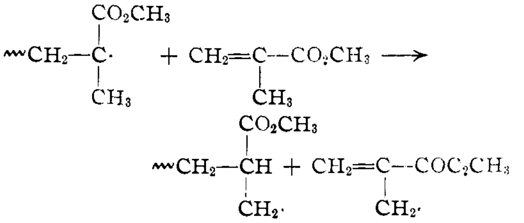
TABLE V

RATE CONSTANTS FOR MONOMER TRANSFER AT 60°

Monomer	$C_m \times 10^5$	k_p	$k_m \times 10^3$	k_m (relative)
MMA	0.7	573	4.0	1.0
Styrene	6.0	176	10.6	2.7
Vinyl acetate	25	3700	925	230

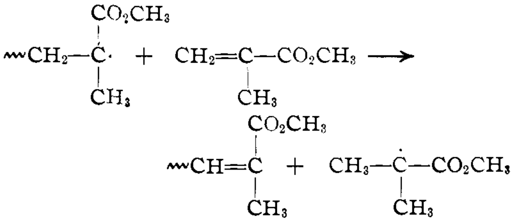
It is seen that the specific rate constants k_m for MMA, styrene and vinyl acetate are in the ratio 1:2.7:230. The relatively large k_m for vinyl acetate is in accord with the extremely high reactivity of poly-(vinyl acetate) radicals known from copolymerization studies.[35] However, copolymerization data suggest that poly(MMA) radicals are *more reactive* than polystyrene radicals. The present observation that the k_m for MMA is *less* than that for styrene (instead of twice as large, as previously reported[34b]) requires some other explanation. We believe that the MMA *molecule* is characteristically inert toward chain transfer, but a detailed rationalization of this view is made difficult by a lack of knowledge of the precise mechanism of the reaction.

Mechanism of the Monomer Transfer Reaction.—While it appears that the observed value of k_m is not incompatible with a conventional *hydrogen abstraction* mechanism (equation 26)



$$\sim CH_2{-}\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot + CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CO_2CH_3 \longrightarrow \sim CH_2{-}\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle CH_2\cdot}{|}}{CH}} + CH_2{=}\underset{\underset{\displaystyle CH_2\cdot}{|}}{C}{-}COC_2CH_3 \qquad (26)$$

the alternative mechanism of *hydrogen donation* (equation 27) must also be considered. However,



$$\sim CH_2{-}\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot + CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CO_2CH_3 \longrightarrow \sim CH{=}\overset{\overset{\displaystyle CO_2CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} + CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\dot{C}}{-}CO_2CH_3 \qquad (27)$$

we must admit that the data permit no conclusion on this point.

Effect of Thiol Structure on Chain Transfer Activity.—In Table VI are listed average values of the transfer constant for the thiols studied.

The greater activity of the aromatic thiols thus is clearly demonstrated, the benzenethiol being about four to five times more active than is 1-butanethiol. This result may perhaps be explained in terms of a resonance stabilization of the

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(27) N. Grassie and E. Vance, *Trans. Faraday Soc.*, **49**, 184 (1953).

(28) J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Polymer Sci.*, **14**, 463 (1954).

(29) On the basis of kinetic and molecular weight data Arnett[5a] concluded that the mechanism of termination of MMA at 50° was predominantly combination. Likewise, his data on the radioactive end group assay and molecular weight of poly(MMA) appeared to support this conclusion.[5b] However, the rate of polymerization at 50° given by Arnett is significantly lower (~15%) than that obtained by Kice and Gratch in this Laboratory, and his molecular weight values are higher than the corresponding values calculated by equation 15. When Arnett's results are re-evaluated in the light of the appropriate revised values of the rate and molecular weight, they are found to be in better agreement with the conclusion that at 50° termination occurs predominantly by disproportionation.

(30) G. S. Hammond, J. N. Sen and C. E. Boozer, papers presented at the 125th Meeting, Kansas City, March, 1954 (Abstracts, p. 14Q), and at the 126th Meeting of the American Chemical Society, New York, September, 1954 (Abstracts, p. 4S).

(31) See H. W. Melville and G. M. Burnett, *J. Polymer Sci.*, **13**, 417 (1954), for a collection of the available data on polymerization rate constants.

(32) It is believed that the factors responsible for this difference are, in order of importance: (a) the previous assumption of termination by combination,[4] (b) differences in the molecular weight relationships,[3] and (c) the previous use of a monomer concentration value of 9.44 moles l.$^{-1}$ instead of the actual value at 60°, which is 8.96 moles l.$^{-1}$.

(33) W. H. Stockmayer, J. T. Clarke and R. O. Howard, Paper presented at the 121st Meeting of the American Chemical Society, Buffalo, March, 1952 (Abstracts, p. 2O).

(34) (a) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 2610 (1949); (b) *ibid.*, **73**, 1700 (1951).

(35) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

TABLE VI

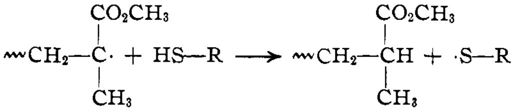
TRANSFER CONSTANTS OF THIOLS WITH MMA AT 60°

Thiol	C_s	Thiol	C_s
2-Naphthalenethiol	(3.1)[a]	2-Mercaptoethanol	0.62
Benzenethiol	2.7	2-Propanethiol	.38
1-Butanethiol	0.66	2-Methyl-2-propanethiol	.18
Ethyl mercaptoacetate	0.63		

[a] This value is relatively uncertain, for reasons discussed in the text.

benzenesulfenyl radical.[36] The increased stability of the radicals derived from the aromatic thiols is also reflected in their ability to produce a slight retardation of the polymerization rate. A related observation is the finding that benzenethiol is about four times more effective than benzyl mercaptan in promoting the degradation of rubber by the cold mastication process.[37] The mechanism postulated for this reaction involves chain transfer of the thiol with polymer radicals produced by the rupture of rubber molecules.[37]

The C_s values for 1-butanethiol (0.66), ethyl mercaptoacetate (0.63) and 2-mercaptoethanol (0.62) suggest that electron-withdrawing substituents may cause a slight *decrease* in the transfer activity of a primary thiol. However, the observed differences are so small that we cannot be certain they are real. In any event, it is clear that polar phenomena[13,35] play a very minor role in the reaction of a thiol with poly(MMA) radicals (equation 28).



$$\sim\!CH_2-\overset{\overset{CO_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\cdot + HS-R \longrightarrow \sim\!CH_2-\overset{\overset{CO_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH}} + \cdot S-R \quad (28)$$

In contrast, Gregg, Alderman and Mayo[11] reported that ethyl mercaptoacetate was approximately *three times more reactive* than a simple 1-alkanethiol toward polystyrene radicals. This result may perhaps be explained in terms of a facilitation of electron transfer from the polystyrene radical to the thiol in the transition state.[13]

The reported decrease in activity of a thiol toward polystyrene radicals which accompanies substitution of methyl groups on the α-carbon atom of the thiol[11] is paralleled here in the series: 1-butanethiol (0.66), 2-propanethiol (0.38), 2-methyl-2-propanethiol (0.18). This appears to be a straightforward example of steric hindrance. However, it is interesting to note that the approximately fourfold decrease in C_s in going from a primary to a tertiary thiol is slightly *less* than the corresponding (sixfold) decrease in the case of the monomer styrene. On the basis of steric considerations alone, a larger relative decrease for the "tertiary" poly(MMA) radical would be anticipated.[38] This result shows the difficulty encountered in attempts to correlate the reaction rates of polymer radicals on the basis of a single theoretical principle.

Acknowledgment.—The authors wish to thank Dr. J. F. Kincaid for his constant inspiration and Dr. T. G. Fox for many helpful suggestions. We are also indebted to Mr. H. Nields for assistance in the experimental work.

[36] H. Z. Lecher, *Science*, **120**, 220 (1954).

[37] M. Pike and W. F. Watson, *J. Polymer Sci.*, **9**, 229 (1952).

[38] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 254–256.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE POLYCHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.' INC.]

Dissymmetry of Molecular Light Scattering in Polymethyl Methacrylates[1]

BY F. W. BILLMEYER, JR., AND C. B. DE THAN

RECEIVED MAY 2, 1955

A new angular dissymmetry light scattering instrument for molecular weight measurements was used in studying the molecular characteristics of polymethyl methacrylates of molecular weights between 35,000 and 10,000,000. Viscosity-molecular weight relations in butanone ($[\eta] = 6.8 \times 10^{-5} M^{0.72}$) and acetone ($[\eta] = 7.5 \times 10^{-5} M^{0.70}$) agreed within experimental error with those reported in the literature. Similar relations in chloroform and ethylene dichloride are not in good agreement with other results, primarily because shear rate corrections were omitted. Polymethyl methacrylates with high molecular weights and broad distributions showed curved Zimm plots associated with polydispersity. These plots could be analyzed to obtain $\bar{r}_z$, $\bar{r}_n$ (the z- and number-average molecular sizes), and $\bar{M}_w$, but not $\bar{M}_n$.

Introduction

During the last decade light scattering has become an accepted and established method for measuring polymer molecular weights. Although several good commercial instruments for making light scattering measurements are available, no one of them, in our opinion, meets all the demands that might be made by workers in today's highly developed field of polymer science. One might ask, for example, for higher sensitivity, freedom from stray light, better angular resolution, more satisfactory optical geometry, easier operation, or more flexibility to meet unusual conditions such as high temperature operation.

This paper describes some studies made with a light scattering instrument which meets many of these demands. The performance of the instrument at room temperature was assessed by measuring the molecular weights and sizes of a series of polymethylmethacrylate samples.

Experimental

Angular Dissymmetry Instrument.—The detailed design of the instrument and its execution were carried out by F. J. Baum and W. H. Aughey[2] to performance specifications as proposed by J. B. Nichols and F. W. Billmeyer, Jr.

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[1] Presented at the 126th National Meeting of the American Chemical Society, New York, N. Y., September 17, 1954.

[2] Chemical Department of the du Pont Company.