[CONTRIBUTION FROM INSTITUTE OF RUBBER RESEARCH, UNIVERSITY OF AKRON]

The Branching Reaction. II. Styrene and Methyl Methacrylate[1]

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A study has been carried out to determine the transfer constants of polystyrene and poly-(methyl methacrylate) in the homopolymerization and graft copolymerization of styrene and methyl methacrylate. This was accomplished by polymerizing the monomers in the presence of varying amounts of the oligomers, and carefully separating the resulting polymers. The effect of oligomer end-groups was determined by using oligomers of different molecular weight (500–5000). As expected, no evidence was found for any chain transfer between styrene radicals and polystyrene, indicating that this transfer constant must be considerably less than 10^{-4}. The values of the other polymeric transfer constants were found to be as listed in Table VIII. These values confirm the expected order of magnitude of the polymer transfer reactions and the expected reactivity and steric factors involved in reactions of these radicals. Any transfer with oligomer end-groups was too low to be detected, hence these values represent the chain-transfer activity of the interior units of the polymer chains. They suggest that branching occurs at very infrequent intervals (about once in ten thousand units) under ordinary conditions.

In the previous paper of this series[2] some results were reported on the possible participation of different initiator radicals in initiating branching during addition polymerization. Since it was found that this branching step was most likely to be started by the growing chain radical itself, the approach used in the present work was to obtain kinetic data on the chain transfer reactions between radicals and polymers in the polymerization of styrene and methyl methacrylate. In ordinary chain transfer measurements, the effect of the transfer agent is determined by observing the change in molecular weight of the polymer (number average)[3] caused by the transfer agent. However, in the case of transfer with the polymer itself, this is not possible, since the new chains grow as branches on the old chains, and there is no net effect on the number-average molecular weight of the total polymer. There is, of course, a broadening in the molecular weight distribution curve, which would be reflected in a higher weight-average molecular weight, which may be measurable.

In order to circumvent this difficulty of separating "old" and "new" polymer, it was decided to use very low molecular weight polymer (oligomer)[4] as the actual transfer agent, since this could then be physically separated from the high polymer formed during the polymerization reaction. This method may be subject to criticism on two points, neither of which, however, comprises a serious objection, when properly handled. The first point concerns itself with the fact that if and when a branching reaction does occur, the oligomer chain is then incorporated into the polymer. While this is true, the additional short chain length cannot seriously affect the molecular weight of the high polymer, if they differ by about two orders of magnitude. The second objection, which is more serious, is concerned with the presence of a large number of end groups in the oligomer. If such groups are involved in more frequent chain transfer than the internal units, they may lead to false values. This objection can, of course, be removed by using oligomer of varying chain lengths and, if necessary, correcting for end-group effects. This approach was used very recently by Schulz.[5] However, his method did not involve actual separation of oligomers and polymers, but measurements of the total contribution of both species.

The work described here includes the measurement of transfer constants of styrene and methyl methacrylate radicals with polystyrene and poly-(methyl methacrylate) in all possible combinations.

Experimental Procedures

Materials.—**Styrene**, supplied by Dow, was freed from inhibitor by distillation under 20 mm. pressure of nitrogen through a 200 mm. Vigreux column to give a product which boiled at 46°.

Methyl methacrylate, supplied by Rohm and Haas, was freed from inhibitor by distillation under 100 mm. pressure of nitrogen, through a 500 mm. Vigreux column, and the fraction boiling at 46° was used. Both monomers were stored under nitrogen in a refrigerator and were used not later than 24 hours after the distillation.

Nitrogen used throughout was Airco high purity.

2,2′-Azobisisobutyronitrile (AIN), supplied by Eastman Kodak Co., was recrystallized from ethanol.

2-Methyl-2-propanethiol, Eastman, was distilled through a 300 mm. column, packed with glass helices, and the fraction which boiled at 63.4–64.0° was used.

Benzenethiol, Eastman, was distilled through a 200 mm. Vigreux column under 15 mm. pressure of nitrogen, and the fraction boiling at 63° was used.

Benzene, J. T. Baker reagent grade, was used in most cases as received. For the cryoscopic molecular weight determinations, it was dried over sodium and distilled. For use as a solvent in polymerizations, the benzene was recrystallized three times and dried over anhydrous calcium chloride.

Acetone and methanol used were both technical grade.

Petroleum benzin, supplied by Merck, had a boiling range of 30 to 60°.

Polymerizations. (a) **Preparation and Characterization of Oligomers.**—A series of oligomers was prepared using thiols as chain transfer agents to obtain the desired molecular weight. In the preparation of the oligostyrenes, 2-methyl-2-propanethiol was used. The calculations of the charge ratios of thiol/styrene used were based on a chain transfer constant of 1.8 at 100° found for this thiol in the course of this work. Oligo-(methyl methacrylate) was prepared using benzenethiol as chain transfer agent, and the value of 2.7 at 60° for the transfer constant.[6]

The polymerizations for the preparation of the oligomers were carried out in a two-liter three-neck flask, equipped with a stirrer, a condenser and a nitrogen inlet-tube. The flask was immersed in an oil-bath maintained at the required temperature ±0.2°. The temperature inside the poly-

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[2] M. Morton, J. A. Cala and I. Piirma, THIS JOURNAL, **78**, 5394 (1956).

[3] F. R. Mayo, *ibid.*, **65**, 2324 (1943).

[4] The term "oligomer" is used, rather than "telomer," in order to facilitate the naming of each type, *e.g.*, "oligostyrene." The prefix itself is in common use in the case of the polysaccharides.

[5] G. V. Schulz, G. Henrici and S. Olive, *J. Polymer Sci.*, **17**, 45 (1955).

[6] J. L. O'Brien and F. Gornick, THIS JOURNAL, **77**, 4757 (1955).

merization flask was checked with a thermometer introduced through the condenser. The flask was first charged with the monomer, followed by the thiol, after the monomer had reached the required polymerization temperature. In the case of methyl methacrylate, where initiator (AIN) was needed, it was added last, dissolved in a small amount of monomer. The polymerization of styrene was carried out at 100° to 10–15% conversion, and the oligostyrene was precipitated in methanol. The filtered oligomer was dissolved in benzene and reprecipitated from methanol. This procedure was repeated two more times to remove any traces of the thiol as indicated by titration with silver nitrate. Methyl methacrylate polymerization was carried out at 60° to 5% conversion. The oligo-(MMA) was precipitated in petroleum benzin, dissolved in benzene and reprecipitated from petroleum benzin. This procedure was repeated three more times. All the oligomers were finely divided powders and were easily dried in a vacuum oven at 40°.

Because of the eventual use of these oligomers as chain transfer agents, they had to be checked for residual thiol, which would obviously have a very drastic effect on the molecular weight of the new polymer. This was done by amperometric titration with 0.002 *N* silver nitrate.[7] Five-g. samples of the oligomers were used for each titration. The oligo-(MMA) was dissolved in 50 ml. of acetone and diluted to 100 ml. with ethanol. The oligomer remained in solution. None of the oligo-(MMA) samples showed any trace of thiol. The oligostyrene samples were dissolved in 20 ml. of benzene. An addition of 80 ml. of ethanol coagulated the oligomer, which had to be removed by filtration, prior to the titration. The oligostyrene samples also showed no trace of thiol. The sensitivity of the amperometric titration method assured a maximum concentration of thiol of about 10^{-7} mole/mole styrene, based on a 1:1 ratio of styrene to oligostyrene in the polymerizing mixture. This is two orders of magnitude smaller than the chain transfer activity of styrene itself, hence it can be assumed that there should be no effect on molecular weight due to any traces of thiol.

The molecular weights of the prepared oligomers were determined by the cryoscopic method. Solutions of each oligomer in benzene were prepared in the concentration range of 5 to 20%. The freezing point depression (ΔT) was determined with a Beckman thermometer. A plot of $\Delta T/C$ *vs.* C was extrapolated to zero concentration, and the molecular weight of the oligomer was calculated with the use of the equation

$$M = \frac{51.2}{(\Delta T/C)_0}$$

where C = concentration in g./100 g. benzene. The measured molecular weights of the oligomers were in good agreement with the expected values as calculated from the disappearance rates of the thiols and their transfer constants. Some examples are given in Table I.

TABLE I

MOLECULAR WEIGHTS OF OLIGOMERS

Oligomer	Mol. wt. Calcd.	Found
Oligostyrene	1150	1210
Oligostyrene	1470	1510
Oligostyrene	2720	2770
Oligostyrene	4450	3620
Oligo(MMA)	1235	1100
Oligo(MMA)	2000	2120
Oligo(MMA)	3200	2930
Oligo(MMA)	4000	5000

(b) Polymerization Reactions.—The polymerizations were carried out in four-ounce bottles, having screw caps lined with extracted butyl gaskets. The bottles were first charged with the oligomer followed by the required amount of benzene. Enough time was allowed for the oligomer to dissolve before the monomer was added. Where initiator was used, it was added last, in benzene solution. The bottles were flushed with nitrogen and placed in an oil-bath maintained at the required temperature ±0.2°. Samples were withdrawn through the perforated caps by means of a hypodermic syringe.

In the polymerizations where oligomer was not present, the % conversion of the polystyrene was determined by dissolving the weighed sample (*ca.* 8 g.) in 30 ml. of benzene and coagulating in 500 ml. of methanol. Similarly the poly-(MMA) samples were dissolved in 30 ml. of acetone containing a little hydroquinone, and coagulated in 500 ml. of methanol/water (90/10) mixture. The precipitated polymer was filtered through a tared fritted glass filter and dried in a vacuum oven at 40°.

The separations of these polymers and oligomers, when oligomers were present during the polymerization, are described separately.

Viscosity and Molecular Weight Determination.—The intrinsic viscosity of each polymer in benzene was determined as previously described.[2] For the polystyrene, the number-average molecular weight was calculated, as before, from the equation[8]

$$\bar{M}_n = 167{,}000[\eta]^{1.37}$$

while the number-average degree of polymerization ($\bar{P}_n$) of the poly-(methyl methacrylate) was calculated by means of the equation of Schuele, Kinsinger and Fox, published by O'Brien and Gornick[6]

$$\bar{P}_n = 2.22 \times 10^3[\eta]^{1.32}$$

Fractionation and Separation of Oligomers and Polymers. **(a) Selection of Solvent–Precipitant Systems.**—Precipitation distribution curves were determined for polystyrene and poly-(MMA) and also for their oligomers, to investigate the possibilities of their separation.

Figure 1 shows the distribution curves for all the polymers and oligomers, in various solvent–coagulant systems. The curves for the oligostyrene and polystyrene show a definite overlapping due to the spread in molecular weight distributions. This is confirmed by the smooth curve obtained for the mixture of the two. Hence a fractionation of the oligostyrene was required. For this fractionation, a 2% solution of the oligostyrene in benzene was used, and the higher molecular weight fraction was precipitated by adding an equal volume of methanol. After 48 hr., the supernatant liquid was removed and coagulated by adding sufficient methanol to reach a final methanol concentration of 80 vol. %. This allowed the low molecular weight ends to remain dissolved. The precipitate then was filtered and dried. All the oligostyrenes were thus treated, and the molecular weights determined cryoscopically.

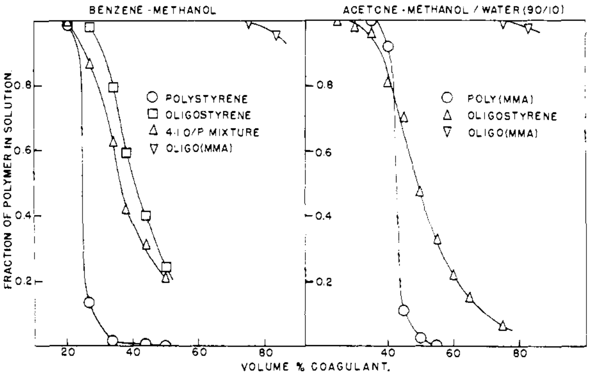

Fig. 1.—Precipitation curves.

Figure 1 also shows the precipitation distribution curves for the poly-(MMA) and the oligo-(MMA) in the acetone–methanol/water (90/10) system. It can be seen that the poly-(MMA) was practically all precipitated at 55 vol. % precipitant and that 75 vol. % precipitant was needed to start the precipitation of the first traces of oligo-(MMA). Hence the separation of the two did not present any difficulties. In the case of the polystyrene–oligo(MMA) the separation also did not present any difficulties, using a benzene–methanol solvent–coagulant system.

The precipitation distribution curves for poly-(MMA) and oligostyrene, however show a complete overlapping

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

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

TABLE II

SEPARATION OF POLYSTYRENE AND OLIGOSTYRENE

(Original soln. contains 0.4100 g. polymer/dl. soln., [η] = 1.90)

Ratio of oligomer to polymer	Recovered polystyrene							
	1st pptn.		2nd pptn.		3rd pptn.		4th pptn.	
	Wt., g	[η]	Wt., g	[η]	Wt., g	[η]	Wt., g	[η]
2.5:1 (mol. wt. = 5100)	0.4207	1.86	0.4078	1.96	0.4140	1.80	0.4106	1.94
	.4410	1.86	.4088	2.00	.4120	1.85	.4102	1.92
8:1 (mol. wt. = 970)	.4188	1.82	.3863	1.98	.3976	1.94	.3532	2.01
8:1 (mol. wt. = 5100)	...	...	.3959	1.99	.3818	2.00	...	...
Polystyrene[a]	.6084	1.92	.6090	1.90	.6100	1.93	.6032	1.90

[a] Original soln. contains 0.6100 g. polymer/dl. soln.

the curves in the acetone–methanol/water system. Similar results were obtained with a benzene–methanol system. It therefore did not appear feasible to separate the poly-(MMA) from the oligostyrene, due to the similarity of their solubility in these systems. Hence it was decided to use a higher molecular weight polystyrene, which would be far less soluble. For this purpose, a polystyrene with number-average molecular weight of 190,000 was fractionated in a 70-30 benzene–methanol system, to remove the lower molecular weight fraction. It was then found possible to separate this polystyrene fraction from the poly-(MMA) in a mixture of the two, by using 10/90 benzene/acetone as solvent and adding sufficient methanol to obtain a final concentration of 45 vol. %.

(b) **Separation of Oligomers and Polymers.**—For the separations of the polystyrene from the oligostyrene, the polystyrene used had an intrinsic viscosity of 1.90 and the two oligostyrenes had cryoscopic molecular weights of 970 and 5100, respectively. The efficiency of separation of these oligostyrenes from the polystyrene was determined using mixtures of oligostyrene, polystyrene and styrene in the proportions which would prevail in actual polymerizations at about 5% conversion of the monomer. These mixtures of monomer–oligomer–polymer solutions were then diluted with benzene so that the final concentration of polymer alone was approximately 0.4 g. per 100 ml. of solution. Eight such solutions were prepared. For the first fractional precipitation, 61.3 ml. of methanol (corresponding to a final vol. % of 38) was added slowly (using a stirrer) to each 100 ml. of solution and they were allowed to settle for at least 48 hours. The clear supernatant liquids were then decanted. Six of the eight oily precipitates were redissolved in 100 ml. of benzene and another 61.3 ml. of methanol was added for a second fractional precipitation. The remaining two precipitates were dissolved in 50 ml. of benzene and the polystyrene coagulated in 500 ml. of methanol. They were filtered and dried in a vacuum oven at 50° and the polymers then were used for intrinsic viscosity measurements. A total of four such precipitations was made and the intrinsic viscosities of the precipitated polystyrenes were determined. The results are listed in Table II.

It can be seen that, in the absence of the oligomer, the recovery of the polystyrene and the reproducibility of the viscosity after each precipitation is excellent within the limits of experimental error of ±0.05 viscosity unit. Similarly, in the presence of the oligomer, the recovery and viscosity of the polystyrene is satisfactory after three or four precipitations. Hence this separation technique was adopted in the polymerization of styrene in the presence of oligostyrene.

For the separation studies of the poly-(MMA) from the oligo-(MMA), the two were dissolved in acetone. Some methyl methacrylate and benzene were added to reproduce conditions which would prevail during an actual polymerization at 2% conversion. Five hundred ml. of this solution was made and divided into 100-ml. portions. For the fractional precipitations, 120 ml. of methanol–water (90/10) was added slowly to each 100-ml. sample, and they were allowed to settle for 24 hours. A total of three such precipitations thus was made and the intrinsic viscosities determined after each precipitation. Using a mixture containing about 0.1 g./dl. of poly-(MMA) ([η] = 4.04) and about 5 g./dl. of oligo-(MMA) (mol. wt. 1850), it was found possible to obtain a sharp separation of the polymer from the oligomer by means of one precipitation.

For the separation of polystyrene ([η] = 1.93) from the oligo-(MMA), a solution of these polymers was made in benzene. The polystyrene was precipitated from the solution at 50 vol. % methanol. The intrinsic viscosities of duplicate samples of the recovered polystyrene (one precipitation) were 1.89 and 1.94, showing satisfactory separation.

For the separation of poly-(MMA) ([η] = 2.73) and the polystyrene fraction ([η] = 1.14) a 10-ml. solution of these polymers was made in benzene and methyl methacrylate, to reproduce conditions which would prevail during an actual polymerization at 2% conversion. Ninety ml. of acetone then was added to this solution, followed by 80 ml. of methanol to complete the precipitation of the polystyrene. The samples were allowed to settle for one week. The supernatant liquid was separated by decantation from the precipitated polystyrene. The poly-(MMA) in the supernatant liquid was precipitated in 500 ml. of methanol–water (90/10). The amount and intrinsic viscosity of the recovered poly-(MMA) after one precipitation were in excellent agreement with those of the original polymer.

Results

Chain Transfer of Styrene with Oligostyrene.—The results obtained when styrene was polymerized in the presence of oligostyrenes of varying molecular weights are shown in Fig. 2 and Table III. The data shown in Fig. 2 indicate that the presence of the oligomer did not have any effect on polymerization rate other than the expected dilution effect. Hence any effect on molecular weight should be due to transfer reactions only.

Table III shows that there is no noticeable effect on the molecular weight of the polystyrene prepared in the presence of the various oligostyrenes (mol. wt. 1000 to 5000). Hence the frequency of chain transfer between styrene radicals and a polystyrene chain must be considerably lower than the 5 × 10^{-4} limit imposed by the kinetic chain length. This finding is in accord with the generally accepted view, based on the viscosity behavior of di-

TABLE III

POLYMERIZATION OF STYRENE IN PRESENCE OF OLIGOSTYRENE

O/M[a]	Mol. wt. of oligomer	Intrinsic viscosity of polystyrene (dl./g.)			
		1st pptn.	2nd pptn.	3rd pptn.	4th pptn.
		Temp. 100°			
0	...	1.92	1.90	1.93	1.90
0.11	1700	...	1.78	1.89	1.90
.25	1700	1.76	1.89	1.90	1.92
.43	1700	...	1.90	1.91	2.04
		Temp. 130°			
	...	...	1.23	1.20	1.16
.25	2800	...	1.10	1.15	1.20
.25	2800	...	...	1.19	1.18
.43	4500	...	1.24	...	1.20
.43	4500	...	...	...	1.21

[a] Base moles oligomer/mole monomer.

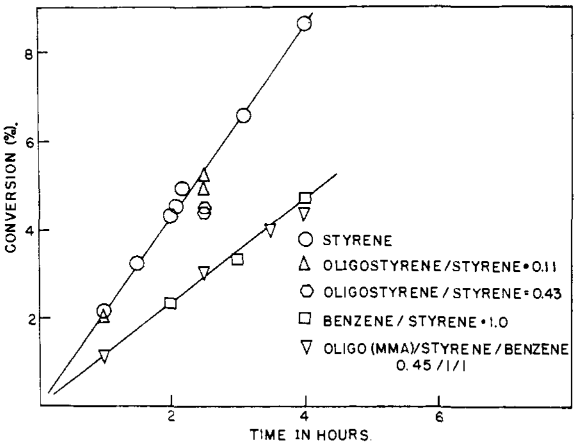

Fig. 2.—Polymerization of styrene at 100°.

lute polystyrene solutions,[9-10] that there is no detectable branching in polystyrene prepared by a free radical mechanism. It is interesting to note that the chain length of the oligomer had no effect on the absence of the branching reaction, indicating that the terminal groups did not participate in any measurable transfer reaction. In the case of the above oligostyrenes, the two types of terminal groups presumably would be a benzyl group at one end and a *t*-butyl sulfide group at the other. None of these apparently is sufficiently reactive to enter into observable chain transfer.

The results obtained with the styrene–oligostyrene system helped also to confirm the accuracy of this method of measuring polymeric chain transfer, including the separation techniques used on the oligomer–polymer mixtures.

Chain Transfer of Styrene with Oligo-(methyl methacrylate).—In the polymerization of styrene in presence of the oligo-(methyl methacrylate), it was necessary to use some benzene as solvent, due to the low solubility of the oligomethacrylate in styrene. Hence all the polymerizations were carried out at a benzene/styrene molar ratio of 1, and the effect of the oligomethacrylate was determined by the usual chain transfer plot. As a precaution and check on the benzene purity, the transfer constant of the benzene was determined at 100° and found to be 1.79×10^{-5}. This agrees very well with the literature value[11] of 1.84×10^{-5}. For the polymerizations at 80°, the transfer constant of 0.59×10^{-5}, calculated from literature data,[11] was used.

The effect of the benzene and the oligomethacrylate on the polymerization rate is shown in Fig. 2 where it can be seen that there is only the expected decrease due to the dilution effect. The transfer activity of the oligomethacrylate at 80 and 100° is shown in Table IV. The plot of $1/\bar{P}_n$ *vs.* *O/M* leads to good straight lines, from which the values of 3.7×10^{-4} and 6.0×10^{-4} were obtained for the transfer constant at 80 and 100°, respectively. These values are well above the limits of experimental error, and can be taken as actually showing the magnitude of the chain transfer activity between a styrene radical and a poly-(methyl methacrylate) chain.

TABLE IV

POLYMERIZATION OF STYRENE IN PRESENCE OF OLIGO-(MMA)

([Benzene]/[Styrene] = 1.0)

O/M	Mol. wt. of oligo-(MMA)	Max. conv. (%)	Rate (%/hr.)	Ave. $[\eta]$	$1/P \times 10^4$	$C \times 10^4$
			80°			
0	...	4.79	0.2	2.99	1.39	3.74
.45	1650	5.67	.2	1.67	3.08	
.69	1900	6.99	.2	1.38	4.00	
			100°			
0	...	4.75	1.16	1.90	2.58	6.04
.26	5000	4.89	1.16	1.34	4.17	
.45	5000	4.41	1.16	1.13	5.27	
.69	5000	4.74	1.09	0.94	6.83	

Chain Transfer of Methyl Methacrylate with Oligo-(methyl methacrylate).—In the polymerization of methyl methacrylate, account must be taken of the well-known Trommsdorff effect,[12] whereby the reaction becomes "autocatalytic" at relatively low conversions. This is presumably due to a marked decrease in the termination rate caused by the rising viscosity of the mixture, the rate constant decreasing, for instance, over 100-fold at 33% conversion.[13] This effect would be of special importance in this work, since the polymerizations are carried out in the presence of oligomer, thereby aggravating any viscosity increase.

In order to check this effect, note was taken of the influence of conversion upon rate and molecular weight. The initiator AIN (2,2′-azobisisobutyronitrile) was used, since thermal polymerization of methyl methacrylate generally leads to erratic results. The initiator charge was kept as low as possible in order to maintain a high molecular weight, which would be more sensitive to chain transfer reactions, even though a higher molecular weight would also aggravate the viscosity increase. The concentration chosen was 4.28×10^{-4} *M* and the effect of conversion on rate is shown in Fig. 3. It is interesting to observe that the

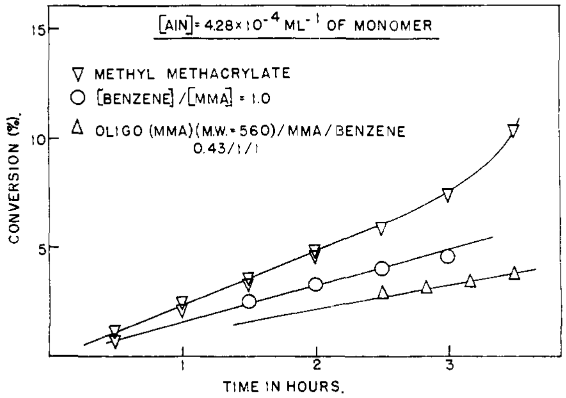

Fig. 3.—Polymerization of methyl methacrylate at 60°.

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(9) (a) C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 477 (1952); (b) O. J. Walker, Jr., and C. A. Winkler, *Can. J. Research*, **B28** 298 (1950).

(10) L. A. Wall and D. W. Brown, *J. Polymer Sci.*, **14**, 513 (1954).

(11) R. A. Gregg and F. R. Mayo, THIS JOURNAL, **75**, 3530 (1953).

(12) E. Trommsdorff, H. Kohle and P. Lagally, *Macromol. Chem.*, **1**, 169 (1948).

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

first noticeable increase in viscosity of the polymerizing mixture occurred at about 6% conversion, which coincides with the beginning of the accelerated rate.

Even though the rate began to increase at this point, no effect was noted on the molecular weight of the accumulated polymer. In view of these results, it at first appeared possible to use this bulk system directly, since the rate was adequate (2.5% per hour), the molecular weight reasonably high, ($M_n = 1.38 \times 10^6$) and the viscosity effect not interfering even up to 10% conversion. However, attempts to carry out such a polymerization in the presence of the oligomer soon showed a downward curvature in the $1/P$ *vs.* O/M plot, indicating a Trommsdorff effect acting to raise the molecular weight of the polymer. Hence all further work was done in the presence of benzene as solvent, leading to satisfactory linear plots.

TABLE V

POLYMERIZATION OF METHYL METHACRYLATE IN BENZENE SOLVENT

S/M	Max. conv. (%)	Rate (%/hr.)	Av. [η]	$1/P_b \times 10^4$
	60°; ([AIN] = 4.28×10^{-4} M.)			
0	5.97	2.50	4.00	0.73
0.5	5.82	1.91	3.68	.81
1.0	4.84	1.65	3.42	.89
1.14	4.02	1.50	3.34	.92
1.32	4.30	1.40	3.28	.94
1.50	4.20	1.38	3.17	.98
1.55	4.36	1.41	3.15	.99
	80°; ([AIN] = 1.34×10^{-4} M.)			
0	6.05	6.75	3.01	1.05
1.28	7.94	3.95	2.56	1.30
1.75	7.07	3.50	2.43	1.40

The effect of the benzene and the oligo-(methyl methacrylate) on polymerization rates is shown in Fig. 3 where the usual rate decrease due to dilution can be observed. Hence the rate effect appears to be in order. The effect of benzene dilution on polymer molecular weight is shown in Fig. 4 and Table V.

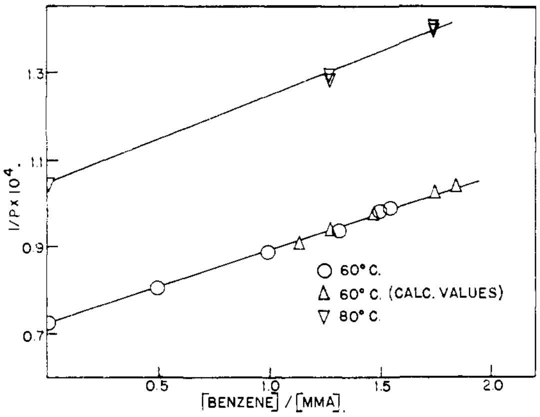

Fig. 4.—Polymerization of methyl methacrylate in benzene.

Since this is a catalyzed polymerization, the molecular weight will be affected not only by chain transfer with the benzene, but also by the dilution effect, in accordance with the expression[5]

$$1/P_b = KI^{1/2}/M + C_m + C_s(S/M) \qquad (3)$$

where

I = initiator concn. (molar)
M = monomer concn. (molar)
S = solvent concn. (molar)
C_m = monomer transfer constant
C_s = solvent transfer constant

Since the initiator/monomer ratio was kept constant in all cases $I^{1/2}/M$ should change, and $1/P_b$ would not be a linear function of S/M. However, Fig. 4 shows very little, if any, departure from linearity and was conveniently plotted in that way. Since C_m for methyl methacrylate at 60° is known, it is possible to determine the value of $KI^{1/2}/M$ at this temperature. This, in the undiluted polymerization at 60°

$$S/M = 0$$
$$C_m = 0.7 \times 10^{-5}$$
$$1/P_0 = 7.25 \times 10^{-5}$$

Hence

$$KI^{1/2}/M = 6.55 \times 10^{-5}$$

In this way, the value of $KI^{1/2}/M + C_m$ may be calculated at any value of S/M. Some of the calculated values are shown in Fig. 4, and it can be seen that they fall very close to the 60° line, if not on the line itself. Hence the contribution of the benzene as chain-transfer agent (C_sS/M) is apparently negligible at 60°, practically all of the change being due to the dilution effect of the solvent on the rates of initiation–termination. This is not surprising, in view of the known low value of the transfer constant for benzene[4] at 60° (0.2×10^{-5}). At 80° this may not be the case, since the transfer constant for benzene[14] is 0.75×10^{-5}. However, this could not be established due to absence of data on the value of C_m at 80°.

The transfer activity of the oligo-(methyl methacrylate) is shown graphically in Fig. 5 and the data are listed in Table VI. It can be seen that, at each O/M value used, the $1/P$ value was corrected for the dilution effect, as obtained from the straight line in Fig. 4, *assuming all of the oligomer to be replaced by benzene, on a volume basis.* The corrected $1/P$ values were then obtained by means of the expression

$$1/P_{cor} = 1/P - (1/P_b - 1/P_0)$$

where $1/P_b$ is the value obtained in the presence of benzene, and $1/P_0$ is the usual value obtained for pure monomer. Hence the $1/P_{cor}$ values in Table VI represent the actual effect of the oligomer as a chain-transfer agent. This treatment ignores the chain-transfer activity of *that portion of the benzene replaced by the oligomer.* This is valid for 60°, where the transfer constant for benzene is very low. However, at 80°, a small correction is applied to the oligomer transfer constant, based on the known transfer constant of benzene (0.75×10^{-5}) and the known volume of benzene replaced by the oligomer at any given O/M ratio.

Chain Transfer of Methyl Methacrylate with Polystyrene.—The same treatment was applied to the polymerization of methyl methacrylate in the presence of polystyrene. The data are shown

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(14) S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc. (London)*, **A202**, 485 (1950).

TABLE VI

POLYMERIZATION OF METHYL METHACRYLATE IN PRESENCE OF OLIGO-(METHYL METHACRYLATE)

O/M	S/M	Mol. wt. of oligomer	Max. conv., %	Rate %/hr.	Av. [η]	$1/P \times 10^4$	$1/P_b \times 10^4$	$1/P_b - 1/P_0 \times 10^4$	$1/P_{cor} \times 10^4$	$C \times 10^4$
60°; ([AIN] = 4.28 × 10^{-4} M.)										
0	0	...	5.97	2.50	4.00	0.73	...	...	...	2.10
.25	1.28	560	4.04	1.17	2.35	1.46	0.94	0.22	1.24	
.43	1.48	560	3.78	1.10	1.95	1.87	0.98	.25	1.62	
.67	1.75	560	3.62	1.13	1.60	2.42	1.02	.30	2.13	
.25	1.28	5000	4.96	1.40	2.35	1.46	0.94	.22	1.24	2.10
.43	1.48	5000	4.60	1.33	1.95	1.87	0.98	.25	1.62	
.67	1.75	5000	4.09	1.24	1.65	2.33	1.02	.30	2.03	
80°; ([AIN] = 1.34 × 10^{-4} M.)										
	0	...	6.05	6.75	3.01	1.05	...	...	...	2.38 2.48 (cor.)
.25	1.28	560	6.99	3.40	1.94	1.88	1.30	.25	1.63	
.43	1.48	560	3.10	2.95	1.64	2.35	1.34	.29	2.06	
.67	1.75	560	6.00	2.80	1.41	2.86	1.40	.35	2.51	

TABLE VII

POLYMERIZATION OF METHYL METHACRYLATE IN PRESENCE OF POLYSTYRENE

(Mol. wt. of polystyrene = 200,000)

O/M	S/M	Max. conv., %	Rate, %/hr.	Av. [η]	$1/P \times 10^4$	$1/P_b \times 10^4$	$1/P_b - 1/P_0 \times 10^4$	$1/P_{cor} \times 10^4$	$C \times 10^4$
60°; ([AIN] = 4.28 × 10^{-4} M.)									
0	0	5.97	2.50	4.00	0.73	...	...	...	2.20
.24	2.28	2.20	0.80	2.16	1.63	1.11	0.39	1.25	
.24	3.28	2.09	.50	1.99	1.82	1.28	.56	1.26	
.41	2.48	0.89	.34	1.83	2.03	1.15	.42	1.61	
.41	3.48	0.89	.20	1.71	2.22	1.32	.59	1.63	
80°; ([AIN] = 1.34 × 10^{-4} M.)									
0	0	6.05	6.75	3.01	1.05	...	...	...	2.86 2.95 (cor.)
.24	3.28	1.57	1.10	1.63	2.36	1.70	.65	1.72	
.41	3.48	1.72	1.10	1.39	2.92	1.74	.69	2.23	

in Table VII and Fig. 6. It should be noted that the separation of the poly-(methyl methacrylate) from the polystyrene introduced some slight difficulties, which had not been encountered in the control separation of the synthetic mixtures. There was a faint turbidity in the supernatant liquid even after centrifugation, apparently due to the solubility behavior of graft copolymers present. It may be expected that the graft copolymers containing the shorter methacrylate chains would precipitate together with the polystyrene, whereas the grafts containing the longer methacrylate chain would remain in solution. Hence, in either case, the supernatant solution would tend to contain a polymer of somewhat higher molecular weight, by virtue of the grafting process. This would tend to decrease the measured transfer constant.

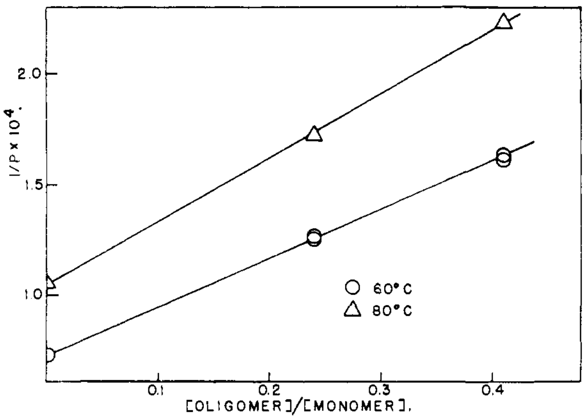

Fig. 5.—Chain transfer of methyl methacrylate with oligo-(methyl methacrylate).

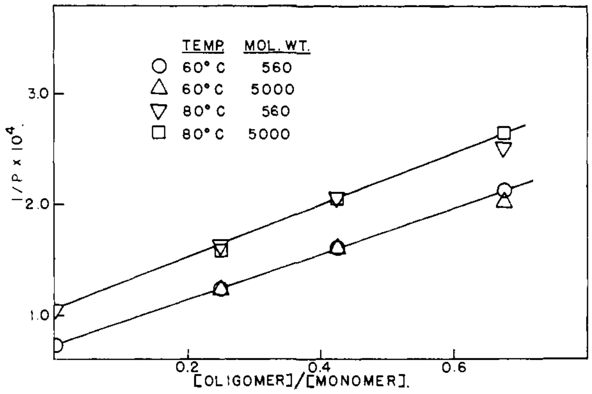

Fig. 6.—Chain transfer of methyl methacrylate with polystyrene.

Discussion

All the values obtained for transfer constants at the various temperatures are combined together in Table VIII, together with the calculated values for the activation energies and frequency factors. In order to obtain the absolute values for the chain transfer reaction (E_{tr} and A_{tr}), use was made of the absolute value for the propagation rate constant, k_p at 60° = 573 l. mole.$^{-1}$ sec.$^{-1}$ for methyl meth-

TABLE VIII

ABSOLUTE CHAIN TRANSFER VALUES

Radical	Polymer	Transfer constants (× 10⁴) 60°	80°	100°	$E_{tr} - E_p$ (kg. cal.)	E_{tr} (kg. cal.)	A_{tr} (l. mole^{-1} sec.$^{-1}$)
Styrene	MMA	...	3.74	6.04	6.35	14.1	6.9×10^7
MMA	MMA	2.10	2.48	...	1.94	8.3	3.1×10^4
MMA	Styrene	2.20	2.95	...	3.43	9.7	3.1×10^5

acrylate[5] and k_p at 100° = 618 l. mole.$^{-1}$ sec.$^{-1}$ for styrene, calculated from Matheson's data,[15] as well as the values of the activation energies, E_p = 6.3 kg. cal. for methyl methacrylate,[13] and E_p = 7.8 kg. cal. for styrene.[15]

The values for the transfer constants are fairly similar for the cases shown, and they differ considerably, in some cases, from the values given by Schulz.[5] The latter actually found a fairly high transfer constant for polystyrene toward styrene (13×10^{-4} at 50°), whereas no transfer whatever was detected here. Such a high transfer constant is not plausible in this case, in view of the marked branching which would result in polystyrene.

An examination of the activation energies and frequency factors elicits some interesting conclusions. Thus the styrene radical appears to be considerably less reactive (higher activation energy) than the methacrylate. This would be expected on the basis of resonance stabilization, and is confirmed by the behavior of these radicals in other reactions, such as polymerization.[16] On the other hand, the methacrylate radical would be expected to have a large steric factor, due to the two substituents on the active carbon atom. This shielding effect is especially noticeable in the reaction between this radical and its own polymer. The frequency factors of 10^4 and 10^5 may be somewhat lower than expected, but they at least indicate the marked steric hindrance experienced by the methacrylate radicals in abstracting hydrogen from the polymer chains.

The transfer activity of these polymers also may be markedly different from solvents of similar structure, *e.g.*, isopropylbenzene as a prototype for polystyrene. Thus Gregg and Mayo[17] have obtained a value of 2.0×10^{-4} for the transfer constant of this solvent with styrene at 100°. On the other hand, Basu, *et al.*,[14] obtained a value of 1.9×10^{-4} for the transfer constant of isopropylbenzene with methyl methacrylate at 80°, a value which is quite close to that found in this work.

It is interesting to compare these data with the behavior of these polymers in thermal degradation at high temperatures. In the latter it has been found[18] that polystyrene degrades largely by chain transfer between radicals and polymer whereas poly-(methyl methacrylate) does so by depropagation of monomers rather than by chain transfer. This does not contradict the findings reported here. It should be noted that the thermal degradation of the polystyrene was carried out at temperatures about 100° higher than those used for the methacrylate. Although a value for the activation energy of the styrene–polystyrene reaction is not available (since no transfer constant was measurable even at 130°), it is obvious that this must be fairly high, considerably higher than the value of 14 kg. cal. found for the styrene–poly-(MMA). Hence at elevated temperatures (*ca.* 300°), it is entirely likely that the polystyrene chains may be even more actively attacked by radicals than the poly-(MMA) chains.

The results shown here confirm the expected order of magnitude of the polymeric chain transfer reactions, and the expected reactivity of styrene and methyl methacrylate radicals. They also indicate that chain branching occurs to only a slight extent, *i.e.*, about once in every ten thousand chain units, under ordinary conditions, in the polymerization or copolymerization of these monomers.

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