strength and behavior of the melts are particularly sensitive to molecular weight and long chain branching.

It now is apparent that many of the differences in behavior of various samples of polyethylene previously attributed to differences in molecular weight distribution are in fact due to differences in short and long chain branching. Nevertheless, there are still unexplained deviations from smooth relationships in the data that have been presented. We feel it is probably due to a combination of the difference in the distribution of molecular weight and long chain branching together with differences in the structure of the crystalline portions of the polymer.[18] Acquiring the understanding needed to explain these apparent anomalies is important. Certainly, as Bryant[17] and Richards[2] have pointed out, the arrangement of the crystalline zones in polyethylene can produce pronounced changes in properties.

In spite of these uncertainties, the significance of the results discussed in this paper extends well beyond the properties of polyethylene. The changes observed in many of the important physical properties due to crystallinity alone, independent of molecular weight, suggest that many of the traditional ideas for the dependence of properties on molecular weight must be revised.

In conclusion, a consistent picture has been presented of the relationships between the molecular structure of polyethylene and various physical and mechanical properties A large portion of the differences between samples is explained by the variation in three independent factors that characterize any sample of polyethylene: namely, the number average molecular weight, the amount of short chain branching and the extent of long chain branching.

Acknowledgment.—The authors wish to express their appreciation to the many individuals in our laboratory who have contributed to this paper: to R. E. Jolly, J. P. Tordella, V. P. Caracciolo and A. E. Symonds who supplied much of the data; to Miss M. T. Dunleavy who performed all of the statistical analyses and especially to D. E. Strain for helpful discussions, guidance and support of all the work discussed in this series of papers.

WILMINGTON, DELAWARE

[18] F. M. Rugg, J. J. Smith and J. V. Atkinson, *J. Polymer Sci.*, **9**, 579 (1952).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Chain Transfer in the Polymerization of Styrene. VIII. Chain Transfer with Bromobenzene and Mechanism of Thermal Initiation[1]

BY FRANK R. MAYO

RECEIVED MAY 23, 1953

The rate and degree of the thermal polymerization of styrene have been studied at 60, 155 and 176° in bromobenzene as solvent, with styrene concentrations from 7.6 to 0.05 *M*. Low molecular weight, saturated, probably cyclic material and higher molecular weight, unsaturated polystyrene seem to be formed in independent reactions, and have been partially separated by precipitation of the higher polymer with methanol. Data on boiling points and unsaturation of dimer and trimer fractions are presented. The low molecular weight saturated polymer results from a non-radical or a biradical reaction, and the saturated dimer is thought to be a diphenylcyclobutane. The high polymer results from an over-all $^5/_2$-order reaction which requires a termolecular reaction of styrene to give two monoradicals. a conclusion consistent with the observed activation energies. There is now no evidence for, and considerable evidence against, any participation of biradicals in the formation of high polymer from styrene. Bromobenzene has about the same reactivity as benzene and chlorobenzene in chain transfer, as measured by the molecular weight of the polystyrene formed. Nevertheless, no significant quantities of bromobenzene are incorporated in the polymer. It is concluded that certain aromatic solvents participate in the chain transfer reaction without permanently combining with the polymer, the net result being chain transfer with the monomer. Two mechanisms for this process are proposed which correlate observations in other polymer and non-polymer reactions.

Previous papers in this series[2] have shown that effects of solvents in decreasing molecular weight in the thermal polymerization of styrene are satisfactorily accounted for by chain transfer with the solvent, at styrene concentrations as low as 0.4–0.6 *M* in cyclohexane, benzene and ethylbenzene and 0.14 *M* in toluene.[3,2a,2c] In the presence of carbon tetrachloride,[2b] carbon tetrabromide,[4] or mercaptans,[2e] the molecular weights of the polymers depend in the same manner on the monomer–solvent ratio, and contain one solvent molecule per polymer molecule. The isolation in good yields and proof of structure of 1:1 products from styrene and carbon tetrabromide or bromotrichloromethane leave no doubt as to the mechanism of chain transfer with these solvents.[5] Further, in every case examined above, the over-all second-order rate constants were nearly independent of monomer concentration and of solvent

However, a single experiment by Breiten-

[1] A preliminary account of this work was presented at the Symposium on Refinements in Polymerization Kinetics at the Buffalo Meeting of the American Chemical Society, March 25, 1952.

[2] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948); (c) R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947); (d) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948); (e) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948); (f) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951); and (g) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953).

[3] (a) H. Suess, K. Pilch and H. Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); (b) H. Suess and A. Springer, *ibid.*, **A181**, 81 (1937); (c) G. V. Schulz, A. Dinglinger and E. Husemann, *ibid.*, **B43**, 385 (1939).

[4] C. H. Bamford and M. J. S. Dewar, *Disc. Faraday Soc.*, **2**, 314 (1947).

[5] M. S. Kharasch, E. V. Jensen and W. H. Urry, THIS JOURNAL, **69**, 1100 (1947); M. S. Kharasch, O. Reinmuth and W. H. Urry, *ibid.*, **69**, 1105 (1947).

bach[6a] was inconsistent with all the other work cited above. By polymerization of 0.1 *M* styrene in chlorobenzene at 153°, he obtained a polymer of molecular weight 410, containing no chlorine. Extrapolation from other experiments in chlorobenzene at lower temperatures[3a] indicated a transfer constant of chlorobenzene at this temperature of about 0.0003, a molecular weight of polymer made in 0.1 *M* solution of 3000–4000 and a chlorine content of about 1% on the basis of one solvent residue per polymer molecule. Since Breitenbach[6a] gave no rates or yields, his work has been repeated and extended, using bromobenzene because of its more convenient boiling point (156°), and some unexpected phenomena have been discovered. Recently, Breitenbach[6b] has reported some similar experiments with chlorinated aromatic solvents at 140°; in these, he obtained much higher molecular weights. With fifty moles of chlorobenzene per mole of styrene at 140°, the polymer averaged 126 styrene units per molecule at 23% conversion. With one chlorobenzene unit per molecule, the polymer should have contained 0.27% chlorine but only 0.1% chlorine was found. Larger discrepancies in chlorine contents were found with other aryl halides, and Breitenbach concludes that reduction of molecular weight by these solvents is mostly a dilution effect, not due to chain transfer.[6b,c]

Experimental

Styrene, N-99, from the Dow Chemical Company, was washed free of inhibitor with aqueous sodium hydroxide, dried, and distilled through a 1-meter packed column at reduced pressure. It was then stored in Dry Ice until used, or else redistilled *in vacuo* just before use.

Bromobenzene from the same source was washed repeatedly with concentrated sulfuric acid and then with water, dried, and distilled through a similar column at atmospheric pressure. A cut boiling within 0.2°, n^{20}_{D} 1.5600, was employed. This material was redistilled through a 50-cm. Vigreux column at about 20 mm. pressure just before use to remove traces of colored products formed in the previous long distillation. This material was used in three sets of runs, starting at the lowest concentration, and adding styrene as needed to the recovered distillate to make further runs at the same or higher styrene concentrations. At the end of a set, styrene was removed from bromobenzene by fractional distillation as above. The recovered material had the original refractive index, was shown to contain 0.02% or less of styrene, and was distilled at reduced pressure before use in the next set. The first run in each set was found to be slow in comparison with the others (no. 28 is included only to illustrate this point), but subsequent runs in all sets gave good agreement both within and among sets. Preliminary runs, with fractional distillation of bromobenzene but without sulfuric acid washing, gave low rates and dark products, but the recovered bromobenzene would give nearly normal results after two cycles. The first product obtained at 0.1 *M* styrene was a black tar containing insoluble material, 7.5% bromine, and less than 0.1% of nitrogen or sulfur. The retarder is therefore probably a hydrocarbon or halogenated hydrocarbon of the same boiling point as bromobenzene. The second product contained 2.5% bromine and was lighter in color. Subsequent rates and products approached those in expt. 32–34, although the maximum molecular weight was attained only slowly.

Procedure.—The styrene and bromobenzene were weighed out in a nitrogen-filled flask; a boiling chip was added, and the mixture was refluxed gently, using a Glas-col heater, and a slow stream of nitrogen at the top of the air condenser, attached by a ground joint. The liquid temperature was determined at intervals so that changes in reflux temperature might be followed and was usually found to be 1.5–2.0° above the vapor temperature. After a suitable reaction time, the condenser was replaced by a 50-cm. Vigreux column and distillation was begun, reducing the pressure to 20–30 mm. and the distillation temperature to around 60° as quickly as possible. The reaction time was measured from the start of active ebullition to reduction of pressure. The concentration of the product was completed in a small distilling flask at about 100° and 1 mm. pressure. The composition of the styrene–bromobenzene distillate was calculated from the amount of polymer obtained, roughly at first, precisely after the products had been purified by precipitation, on the assumption that evaporation and mechanical losses, usually below 0.5%, caused no change in ratio. This assumption was checked by analyses of the distillates from expts. 34, 36 and 38 for unsaturation; the calculated and experimental styrene contents agreed within the accuracy of the method (about 1%). Additional styrene was then added and the next run was started directly. Runs were carried out in the sequence indicated by their numbers.

Experiments 37 and 38 were carried out with a Vigreux column as reflux condenser and the liquid temperature was followed continuously. Experiment 20 was carried out in a sealed, evacuated, tube containing an Anschütz thermometer. The tube was suspended in vapor from vigorously boiling bromobenzene (155.2°), then cooled in water. Since an unrecorded experiment showed considerable superheating, tube no. 20 was agitated by twisting it back and forth by an extension on the tube, and the maximum temperature reached was 158.7°. In expt. 20, 37 and 38, reaction times for numerous short intervals above 100° (135° for no. 20 where heating and cooling were faster) were converted to their equivalents at 155°, using an activation energy of 21 kcal./mole for the over-all reaction. Thus 9 minutes between 135 and 158.7° for no. 20 is treated as 10.54 minutes at 155° in Table I, and 50 minutes at 100–154.8° for no. 38 is taken as 40.46 minutes at 155°.

In the recorded experiments, polymer yields were calculated approximately from the weights after concentration as above, in order to assure consistency in rates and to start the next experiment before purifying the polymer. Suitable residues were later combined and precipitated several times as follows. The polymer was dissolved in 1–2 volumes of reagent benzene and reagent methanol was added until no more precipitate formed. The solvents were then decanted and the polymer was washed thoroughly with two portions of methanol, while the polymer was kneaded with a spatula. Solution and precipitation were then carried out twice more in the same manner. All the liquors and washings were then concentrated, first by evaporation by warming, finally by heating the residue to about 100° below 1 mm. pressure to remove any traces of bromobenzene and styrene as well as solvents. This residue was largely insoluble in pure methanol. High polymer in this residue (of which the dry weight was about one-third the recorded weight of the low fraction) was precipitated three times from benzene by methanol by the procedure above and then combined with the previous larger lot of polymer, the combination being designated as the high (H) fraction in Table I. The liquors were concentrated as before and the light brown oil obtained is designated low (L). The L fractions thus contain polymers soluble in both series of precipitations, and were found to be nearly uniform in molecular weight whenever enough was obtained for investigation. Other L fractions are assumed to have the same molecular weight.

In working up the combined products of expt. 29–31, 145 ml. of methanol and 45 ml. of benzene were used. Evaporation of these quantities of solvents left 0.7 mg. of brown, resinous residue, not enough to affect most recorded results. Appropriate corrections ($\sim$ 2%) have been made with low fractions of no. 20 and the 60° run.

Bromine analyses were made by the Clark Microanalytical Laboratory, by combustion of large samples in the case of polymers. 20H, prepared from a different lot of styrene in the absence of bromobenzene, mol. wt. 116,000, 0.18% halogen as Br, and 38H, prepared with 1.6 *M* styrene in bromobenzene, mol. wt. 50,200, 0.42% Br, serve as blanks. 29–31 were prepared from 0.05 *M* styrene, with the highest proportion of bromobenzene. The high fraction, mol. wt. 1,550, contained 0.44% Br, essentially the same as the

---

[6] (a) J. W. Breitenbach, *Naturwissenshaften*, **29**, 708, 784 (1941); (b) *Makromol. Chem.*, **8**, 147 (1952); (c) J. W. Breitenbach and H. Karlinger, *Monatsh.*, **82**, 245 (1951).

blank. The oily low fraction, mol. wt. 356, contained 1.38% Br, corresponding to an average of 0.061 atom of bromine per molecule. In view of the observation that 5 days of refluxing of bromobenzene without styrene left 0.003% of oily residue, presumably high in bromine, all the bromine in expt. 29–31L might have arisen from this source. The conclusion that even the lowest molecular weight polymers contain little or no bromine arising from polymerization or chain transfer processes is fully corroborated by many other analyses on experiments not recorded here.

The possibility that no bromine was found in the products because hydrogen bromide had been lost has been excluded. An experiment like 28 with 3278 g. of bromobenzene gave 1.37 g. of L + H polymer with an average molecular weight of 662. This polymer contained 0.5% Br, 0.38% more than the blank on the monomer used, corresponding to incorporation of 6.5×10^{-5} equivalent of bromine in 2.07×10^{-3} mole of polymer (0.0314 bromine/molecule). All the nitrogen used to maintain an inert atmosphere during the polymerization was passed through water, in which only 1.1×10^{-5} mole of bromine ion was found (0.0053 HBr/polymer molecule). No solvents were employed in the isolation of polymer and all the late stages of removal of styrene and bromobenzene *in vacuo* were carried out with a liquid nitrogen trap in the vacuum line. Titration of the trap contents showed the presence of only 4×10^{-6} mole of acid, corresponding to 0.0019 HBr/polymer molecule. The final distillates were collected and redistilled. They boiled in a very narrow range, with no evidence of any phenylethyl bromide (boiling about 50° above bromobenzene). The total halogen found in the polymer (beyond the blank) and evolved is thus only 0.039 equivalent per polymer molecule formed.

Molecular weights were determined cryoscopically in benzene by Mrs. P. Morrison. Samples were chosen to give a depression of about 0.2° and the depression constants were determined on each lot of specially purified benzene using triphenylmethane as standard. Intrinsic viscosities were determined in benzene at 30° with flow times near 200 seconds[2b]: 20H, 0.765: 37H, 0.398; 38H, 0.433; 35–36H, 0.167; 32–34H, 0.071; A-H, 3.63. These were converted to number average molecular weights by the relation[2f]

$$\overline{M}_n = 167000[\eta]^{1.37} \qquad (1)$$

Analyses for unsaturation were carried out by treating the samples, alone or in 2–5 ml. of carbon tetrachloride, with 10 ml. of $N/10$ bromine in carbon tetrachloride for 10 and 20 min. in glass stoppered flasks in the dark, and the amount of addition found for polymer samples showed no trend with these reaction times. One ml. of saturated aq. potassium iodide and 25 ml. of water were then added (shaking after addition of first 2–3 ml. to absorb hydrogen bromide from vapor phase) and the solution was titrated with $N/10$ sodium thiosulfate using a 10-ml. buret. When the end-point was reached, corresponding to unreacted bromine. solid potassium iodate was added and hydrogen bromide was determined by further titration of iodine.[7] By comparison with blanks on the bromine solution, the number of equivalents of bromine reacting by addition is equal to the decrease in equivalents of thiosulfate consumed before addition of potassium iodate minus twice the increase in equivalents of thiosulfate consumed after addition of iodate. The first term corresponds to the bromine reacting by both addition and substitution, and the second term to substitution only. Sample sizes were chosen so that about 50% of the bromine would react by addition and 50–90% of the bromine commonly reacted by addition and substitution together. The validity of the method was established by tests with styrene, α-methylstyrene and with a polymer corresponding to 32-34A. One-ml. aliquots of a 0.29 *M* solution of styrene in carbon tetrachloride analyzed for 0.973, 1.010 and 1.010 double bonds per styrene after 1.0, 2.0 and 14.5 hours, with no substitution. Bromine solutions containing traces of hydrogen bromide reacted faster. One-ml. aliquots of a 0.28 *M* solution of α-methylstyrene in toluene (to allow for the large number of easily substituted benzyl hydrogen atoms in polystyrene) analyzed for 1.005 and 1.022 double bonds per molecule after 24 and 120 minutes reaction, respectively, although the amount of substitution doubled in the longer time. A polymer like 32-34A gave similar results with a range of sample sizes and reaction times (results are expressed as g. of sample required to add one mole of bromine): 0.8-g. sample for 10 minutes, 3337; 0.2-g. sample for 20 min., 3281. Extensive substitution occurred in both tests.

Concentrations of styrene in bromobenzene at 155° were calculated using 1.3070 for the density of bromobenzene[8] and 0.79 for styrene. An experimental determination of the density of styrene, good to about 0.5%, from the initial volume of a run like no. 20, gave the value 0.788 at 156°.

Results and Discussion

Experimental data are summarized in Table I. Experiment 28 was the first carried out with the bromobenzene used for all experiments; since it was considerably slower than 29–31, and since subsequent runs in all sets gave better checks, it is assumed that polymerization 28 served mostly to purify the solvent.

Rates of Polymerization.—Over-all rate constants for the thermal polymerization of styrene in Table I are based on the total amount of polymer formed, including the portion which is not precipitated by methanol (L fraction) and which has usually been neglected in previous work. The table shows that this soluble fraction comprises only 1.5–2.7% of the total product at styrene concentrations studied previously at lower temperatures, but up to 25% in the most dilute solutions. When the high (H) and low (L) molecular weight fractions are considered separately, the reaction order is much closer to 5/2 than to two or three for the high fraction; closer to two for the low fraction. Since extraction of the low from the high fraction probably becomes less complete as the proportion of low fraction becomes very small, and since the L fractions contain low molecular weight unsaturated chain transfer products as well as saturated molecules apparently arising from non-radical reactions, the rates and reaction order for low fractions are of limited significance. However, the effects of these errors on results for the predominant H fractions will be small.

The data show that over the concentration range which has been studied most at lower temperatures, above 1 *M*, the formation of high polymer is represented better as a second- than as a 5/2-order reaction, and that above 0.4 *M*, second order is as good as 5/2. The general conclusion[2,3] that the over-all thermal polymerization is second order is thus accounted for. On the other hand, over the more than thirty-fold concentration range from 0.05 to 1.6 *M* styrene, the rate of high polymer formation agrees much better with the five-halves order relation (compare second- and 5/2-order over-all rate constants and $k_{5/2}$ for high fractions). The most plausible explanation is that the reaction is 5/2 order, but that in the transition from pure styrene to its solution in a number of common solvents there is an increase in over-all rate constant which makes the reaction appear to be second order over this range.

Table II summarizes one experiment, carried to 71% conversion from an initial styrene concentration of 0.4 *M*, from which samples were withdrawn at intervals. There is not much choice between

---

[7] H. P. A. Groll, G. Hearne, F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939).

[8] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. 1, Julius Springer, Berlin, 1923, p. 273.

TABLE I

THERMAL POLYMERIZATION OF STYRENE IN BROMOBENZENE

Expt. no.	Reactants (g.) C_8H_8	Reactants (g.) C_6H_5Br	$[C_8H_8]_0$^{a} moles/l.	$C_6H_5Br^{b}/C_8H_8$	Reaction Time, hr.	Reaction Temp., °C.	Yield G.	Yield %	Over-all rate constants^{c} × 10^6, (L + H), calcd. to 155° k_2	$k_{5/2}$	k_3	Wt. frac., g.	% L frac.	Mol.^{d} wt.	k_2 × $10^{6\,e}$ L frac.	$k_{5/2}$^{e} × 10^6 H frac.
20	13.33	0	7.58	0	0.176^{f}	155	1.86	13.96	33.9	12.8	4.83	L0.029	1.56	.....	0.53	.....
												H1.83	...	116000^{d}	.....	12.5
38	33.17	197.3	1.65	4.21	0.674^{f}	155	4.10	12.35	35.3	28.3	22.8	L0.165	1.73	.....	0.58	.....
37	32.53	199.9	1.61	4.45	1.02^{f}	155	5.43	16.69	33.9	28.1	23.1	H9.36	...	50200^{d}	.....	27.5
36	51.10	1480	0.410	20.33	4.17	157.2	5.62^{g}	11.00	17.5	28.6	46.1	L0.30	2.71	361	0.47	.....
35	50.95	1489	.406	20.48	4.02	157.5	5.43^{g}	10.66	17.6	28.3	46.1	H10.75	...	14360^{d}	.....	27.5
														4503		
34	33.33	3991	.1034	84.2	42.0	157.3	3.83^{h}	11.49	7.25	23.2	75.3	L1.51	13.7	306	1.00	.....
33	33.18	4001	.1027	84.5	40.0	156.8	3.56^{h}	10.73	7.28	23.6	75.3	H9.49	...	4460^{d}	.....	20.6
32	32.78	4015	.1010	85.9	40.0	157.2	3.61^{h}	11.01	7.53	24.3	79.5			2640		
31	16.66	4030	.0515	172.7	161	157.0	2.38^{i}	14.29	4.97	22.9	104	L1.85	24.9	356	1.36	.....
30	16.52	4041	.0509	175.7	160	156.6	2.54^{i}	15.28	5.67	25.0	119	H5.58	...	1549	.....	18.6
29	16.52	4058	.0508	176.2	157	156.8	2.51^{i}	15.19	5.67	26.0	121					
28	16.49	4100	.0501	175.9	166	158.1	2.05^{i}	12.43	3.97	18.5	84.7					
A	31.04	0	8.35	0	96.0	60.0	2.51	8.08	^{j}0.0303	^{j}0.0109	^{j}0.0038	L0.022	0.90	.....	^{j}0.00027	.....
												H2.49	...	980000^{d}	.....	^{j}0.0108
22	7.22	1762	0.0497	161.5	47.5	176	0.54	7.47	9.45^{k}	44.5^{k}	206^{k}	.....	...	.....	.....	.....
														.....	.....	.....

[a] Initial concentration of styrene at 155° (at 60 and 176° in last two experiments). [b] Average mole ratio. [c] Second, five-halves, and third-order rate constants for L + H fractions were calculated from the equations, $k_2t = 1/[M] - 1/[M]_0$, $1.5k_{5/2}\,t = 1/[M]^{3/2} - 1/[M]_0^{3/2}$, and $2k_3t = 1/[M]^2 - 1/[M]_0^2$, where [M] and $[M]_0$ are the initial and final concentrations of styrene in moles/l. at reaction temperature and t is time in seconds. [d] Molecular weights by freezing point in benzene, except values marked "*d*" are from intrinsic viscosity and eq. 1. [e] Taken as the proportion of that fraction in total polymer times the appropriate over-all rate constant. [f] Calculated for 155° as described in the experimental part. [g-i] Weights of these heated but not precipitated polymers were corrected to these values, using the average weight loss for each group on precipitation. The original whole polymer lost 7.92%,[g] 6.94[h] and 6.19[i] of retained solvent during the precipitation procedures. Expt. 28 is corrected but not fractionated; expt. 22 is neither fractionated nor corrected. [j] 60°. [k] 176°.

5/2- and third-order rate constants, but the rates at low conversions agree well with those in expt. 35–36, and a second-order over-all reaction is excluded.

Temperature Coefficients.—From $k_{5/2}$ for the high fractions of expt. A and 20, with time units in seconds

$$k_{5/2} = 6.91 \times 10^{\cdot} \exp(-21020/RT) \quad (2)$$

For the conventional second-order propagation and termination reactions, an over-all 5/2-order reaction corresponds to a third-order initiation.

From Matheson's values of the propagation and termination constants[9]

$$k_p = 2.16 \times 10^7 \exp(-7760/RT) \quad (3)$$

$$2k_t = 2.59 \times 10^9 \exp(-2370/RT) \quad (4)$$

and the relation $k_{5/2} = k_p(k_{3i}/k_t)^{1/2}$, the third-order initiation constant is

$$k_{3i} = 1.32 \times 10^6 \exp(-28900/RT) \quad (5)$$

and although the value is probably not exact, it should be of the right order of magnitude.

The over-all rates of polymerization in the absence of solvent at both 60 and 155°, are consistent with previous work,[2c,f,10] and the calculated activation energy is essentially the same for a five-halves as for a second-order reaction.

The transfer constant of styrene with styrene, C_m, is 6 × 10^{-5} at 60°.[2f] Schulz has shown that styrene behaves much like ethylbenzene in transfer,[11] and the temperature coefficient for ethylbenzene[2c] leads to the estimate that $C_m = 4 \times 10^{-4}$ at 155°. The transfer constant of benzene at 155° is calculated to be 2.4 × 10^{-4}.[2c] Since the transfer constant of chlorobenzene at 100° is 1.3 that of benzene,[2a] the transfer constant of chlorobenzene at 155° should be about 3.1 × 10^{-4}.

From the molecular weights of 20H and AH, prepared at 158 and 60°

$$1/\overline{P} = 1.25 \exp(6200/RT) \quad (6)$$

The indicated activation energy for the chain termination is in the range of previous values,[10] somewhat closer to that calculated for chain transfer with the monomer as the limiting

---

(9) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

(10) L. C. Rubens and R. F. Boyer, Chap. 7 in R. H. Boundy and R. F. Boyer (editors), "Styrene," Reinhold Publ. Corp., New York, N. Y., 1952. A more recent paper in the field is by M. F. Vaughan, *J. Appl. Chem.* (*London*), **2**, 422 (1952).

(11) G. V. Schulz, "The American Fiat Review of German Science," Vol. 35, The O. W. Liebiger Research Laboratories, Inc., Petersburg, N. Y., 1950, p. 155.

TABLE II

POLYMERIZATION OF 0.4 *M* STYRENE IN BROMOBENZENE AT 158.6°[a]

Time, hr.	Polymerization, %	Over-all rate constants $\times 10^6$ at 155°[b] $k_{5/2}$	k_3
2.04	6.26	29.6	47.9
4.03	11.62	30.3	50.4
8.01	19.8	28.2	48.8
24.00	36.9	22.4	42.5
48.00	50.2	20.8	44.1
80.00	59.8	20.3	47.9
144.00	70.6	21.9	59.2

[a] Started with 2000 g. of bromobenzene (from expt. 34) and 67.33 g. of styrene. Samples containing about 1 g. of polymer were withdrawn and concentrated by distillation, finally heating to 140° at 0.3 mm. for 5 min. These residues lost an average of 2.8% of (presumably) styrene and bromobenzene on reprecipitation and conversions have been corrected accordingly. The first three runs together gave 4.2% low polymer, the last three, 6.0%, but over-all rate constants include high and low fractions. [b] Calculated for the period since last previous sample was taken, and corrected to 155° by dividing by 1.23. Units are moles, liters and seconds.

step than to that calculated for chain initiation and radical interaction.

The over-all second-order rate constant for the formation of the low-molecular weight oily fractions is found from expt. A and 20.

$$k_2 = 1.8 \times 10^5 \exp(-22600/RT) \qquad (7)$$

The accuracy of this relation depends mostly on the efficiency of the fractionation process; since it is not here complicated by solvent reactions, it should be of the right order of magnitude.

Molecular Weights and Chain Transfer with Bromobenzene.—Previous determinations of transfer constants in the thermal polymerization of styrene[2] have been based on a second-order initiation, a second-order over-all reaction, and the equation

$$\frac{1}{\bar{P}} = \frac{C[\text{S}]}{[\text{M}]} + \frac{1}{\bar{P}_0} \qquad (8)$$

where $\bar{P}$ and $\bar{P}_0$ are the average degrees of polymerization of styrene, [M], in the presence and absence of solvent, [S], and where C is the transfer constant of the solvent at the temperature employed. First we shall determine the transfer constant of bromobenzene by this relation and then we shall consider the effect of the third-order initiation and 5/2-order over-all reaction proposed in the present paper.

Figure 1 plots $1/\bar{P}$ for high molecular weight (H) fractions against bromobenzene–monomer ratios. For consistency with previous work, number average molecular weights have been determined from intrinsic viscosities and the methanol-soluble (L) fractions have been neglected.[12] For the solvent:monomer ratios of 4.3, 20.4 and 85, C = 2.7, 3.1 and 2.6 × 10^{-4}, respectively. Molecular weights determined cryoscopically are considerably lower than number average molecular weights determined viscometrically, indicating an unusually broad molecular weight distribution, possibly due to unextracted low fractions. Nevertheless, transfer constants calculated from cryoscopic molecular weights at 85 and 175 mole ratios are 4.5 and 3.8 × 10^{-4}, of the same order as the other values. A transfer constant for bromobenzene of 3 × 10^{-4} at 155° is entirely consistent with values estimated in the previous section, 2.4 × 10^{-4} for benzene, 3.1 × 10^{-4} for chlorobenzene.

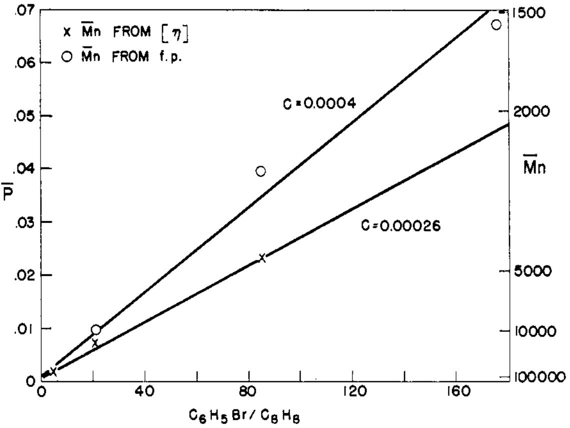


Fig. 1.—Thermal polymerization of styrene in bromobenzene at 156°.

The effect on these results of introducing a third instead of a second-order[2a] initiation reaction is small. The following equation is easily derived, assuming termination by combination of radicals.[2f,13]

$$\frac{1}{\bar{P}} = C_\text{m} + \frac{C[\text{S}]}{[\text{M}]} + (k_{3\text{i}}k_\text{t}[\text{M}])^{1/2}/k_\text{p} \qquad (9)$$

The last term is equal to $k_{3\text{i}}[\text{M}]^{1/2}/k_{5/2}$; all the constants are therefore known fairly well and at 155°

$$\frac{1}{\bar{P}} = 0.0004 + \frac{0.0003[\text{S}]}{[\text{M}]} + 0.00018[\text{M}]^{1/2} \qquad (10)$$

For expt. 20, without bromobenzene and with an average value of [M] = 7.05, the calculated value of $1/\bar{P}$ is 0.00088, in excellent agreement with the observed 0.00090. If in using this relation to calculate the transfer constant of bromobenzene at 156–158°, we substitute 0.0004 + 0.00018$[\text{M}]^{1/2}$ for $1/\bar{P}_0$ (= 0.00090) in the original equation, then the calculated transfer constants at bromobenzene–styrene ratios of 4.33, 20.4 and 85 are 3.3, 3.3 and 2.7 × 10^{-4} instead of 2.7, 3.1 and 2.6 × 10^{-4}. Thus, the correction is largest for points nearest P_0, but even for this representative of the least reactive solvents, the correction is small. In view of the fact that the over-all reaction is nearer second than 5/2-order in the range where the correction for 5/2-order is largest, it is doubtful that the correction is worth making at all at 155°.

The corresponding equation for 60° is

$$\frac{1}{\bar{P}} = 6 \times 10^{-5} + \frac{C[\text{S}]}{[\text{M}]} + 1.26 \times 10^{-5}\,[\text{M}]^{1/2} \qquad (11)$$

The calculated value of $1/\overline{P}$ for expt. A is 9.6

---

(12) If the transfer constant is calculated on combined L and H fractions of all runs instead of only on H fractions, the transfer constant is then about twice as large; however, the results are then not comparable with previous work and evidence will be presented that much of the low polymer arises from a different mechanism.

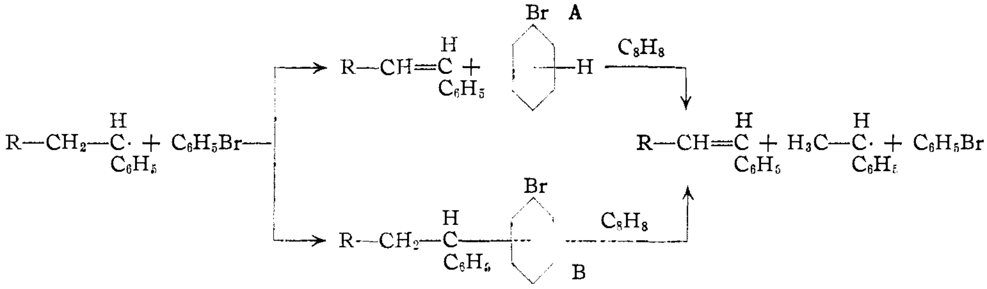
(13) If chains end mostly by disproportionation at 155°, then the last term has a factor of 2 in the numerator and the k_t is probably not the one measured in ref. 9. The coefficient of the last term in eq. 10, however, agrees with the experimental value in the absence of solvent.

$\times 10^{-5}$ while the experimental value is 10.6×10^{-5}. Application of suitable corrections to data on hydrocarbons at 60°[2c,14] showed that with ethylbenzene, the spread in the individual values of C was reduced by one-third and that the average value was increased from 6.7 to 7.6×10^{-5}. Less reactive solvents require relatively larger corrections, and with more reactive solvents the correction becomes unimportant, but because the over-all reaction order is very close to second order in the solvent:monomer ranges covered by these experiments, it is uncertain whether the corrected (to 5/2 order) or uncorrected transfer constants are more accurate.

The Mechanism of Chain Transfer with Aromatic Solvents.—Although the effect of bromobenzene in reducing the molecular weight of polystyrene is the same as that of benzene and chlorobenzene, neither bromine nor phenyl groups from bromobenzene are incorporated in the polymer in significant quantities. Since with both this and other types of solvents, $1/\bar{P}$ is a linear function of the solvent:monomer ratio, it is hard to escape the conclusion that bromobenzene somehow participates in the transfer step. Breitenbach has proposed that the decrease in molecular weight without incorporation of solvent is purely a dilution effect,[6b,c] but this proposal seems untenable unless we abandon the conventional second-order propagation and termination reactions. For a second-order initiation and a second-order over-all rate of polymerization, dilution by a perfectly inert solvent will have no effect on the molecular weight. For a third order initiation and a 5/2-order over-all reaction, with which we seem to be dealing, dilution with an *inert* solvent will *increase* the molecular weight, the molecular weight being finally limited only by transfer with the monomer. For the molecular weight to *decrease* with decreasing concentration of monomer, the initiation must be of lower order than second. First- and zero-order initiations require over-all 3/2- and first-order kinetics, in disagreement with experiment[2]; they also seem to require too high activation energies.

Three other explanations for the effect on molecular weight of dilution with bromobenzene at 155° have been considered and rejected. The effect is not due to approach to a ceiling temperature.[15] First, the over-all rate is consistent with data at other temperatures.[2c,f,10] Second, expt. 22 at 176° reacted twice as fast as expt. 28–31 at 156–158° and so 176° is still below the ceiling temperature (though perhaps not much below at the low monomer concentration used). In general, depropagation reactions are unimportant 20° below the ceiling temperature. Neither is the effect due to thermal cracking of polystyrene on long heating in bromobenzene. A solution of 3.12 g. of 38H polystyrene, intrinsic viscosity 0.433, was refluxed in 780 g. of bromobenzene for one week at 157°. This solution was 0.05 M in styrene units. 3.08 g. of solvent-free polymer was recovered with intrinsic viscosity 0.400. From eq. 1, the molecular weight decreased from 53,100 to 47,600, corresponding to a loss of only 0.23 bond per thousand styrene units per week at 157°. Finally, the consistency of the rates in bromobenzene at moderate dilutions with rates in other solvents, and the excellent reproducibility of duplicate experiments at the highest dilutions, with recycling of bromobenzene, seem to exclude effects of accidental catalysts and inhibitors.

To account for chain transfer with bromobenzene without incorporation of this solvent in the polymer, two mechanisms are proposed



(12)

The hydrogen atom or substituted benzyl radical may be either complexed with the aromatic solvent or directly bonded to an aromatic carbon atom. In the second step, the bromobenzene is set free (possibly with an exchanged hydrogen atom) and the net result is chain transfer with the monomer. Since benzene and chlorobenzene have about the same reactivity as bromobenzene, the halogen atoms seem not to be involved in the complex. The activation energy for chain transfer of styrene *via* benzene[2c,9] is 22.6 kcal./mole. This value, and the failure of aromatic hydrocarbons and halides to affect the over-all rate constant of polymerization, indicate that the first step in either two-step sequence is rate-determining.

There is ample evidence that free radicals can add to aromatic compounds to give products which are still free radicals. Benzene, toluene and chlorobenzene retard the polymerization of vinyl acetate,[16,17] although phenyl radicals should continue chains readily.[18] Several polynuclear hydrocarbons retard the polymerization of styrene and the addition of bromotrichloromethane to styrene.[19] Naphthalene retards the photochemical side-chain

---

(14) The last term was taken as $2 \times 10^{-5} [M]^{1/2}$ to be consistent with the value of $1/\bar{P}_0$ used in the earlier paper.

(15) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 331 (1950).

(16) W. H. Stockmayer and L. H. Peebles, THIS JOURNAL, **75**, 2278 (1953).

(17) G. M. Burnett and H. W. Melville, *Disc. Faraday Soc.*, **2**, 322 (1947).

(18) M. J. S. Dewar, *ibid.*, **2**, 368 (1937); W. A. Waters, "Chemistry of Free Radicals," Oxford University Press, 1948, p. 146.

(19) M. Magat and R. Bonême, *Compt. rend.*, **232**, 1657 (1951); E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

bromination of toluene without much bromination of the naphthalene.[20] In these reactions, the radical or atom is apparently converted to a more stable radical by reaction with the aromatic solvent, increasing the chances of chain termination over propagation. Further, phenyl radicals from several sources react with monosubstituted benzenes to give biphenyls with one and only one substituent,[21] proving that the phenyl radicals react with the solvents without liberating solvent radicals. If styrene radicals react with bromobenzene by mechanism 12B, there can be no significant ejection of hydrogen atoms[21b,c] from the substituted benzyl radical–solvent complex, because solvent does not appear in the polymer. Although energy relations may be different in phenyl radical–aromatic solvent complexes,[22] the conclusion that the hydrogen atom is retained in such complexes until an acceptor is found seems energetically more probable. These considerations suggest that the concerted reactions of two radicals with reagents proposed by Hammond and co-workers[23] in their study of the decomposition of benzoyl peroxide by triphenylmethyl involve instead complexed radicals.

The recent communication by Stockmayer and Peebles[16] has shown that vinyl acetate copolymerizes with benzene at 60°, and therefore that the free radical formed from the vinyl acetate radical and benzene adds to vinyl acetate. In the present work with styrene at 155–160°, the complex reacts with styrene by transfer of a hydrogen atom rather than by addition. Since styrene is usually 50–100 times as reactive as vinyl acetate toward addition of a given radical,[24] either the transfer reaction has a higher temperature coefficient than addition, or the complexes formed with aromatic solvents by styrene radicals and vinyl acetate radicals are fundamentally different, or both. Perhaps the high temperature transfer reaction proceeds through the complex 12A, while a low temperature addition reaction proceeds through the complex 12B. With styrene, only the transfer reaction has been observed thus far with benzene derivatives, although copolymerization has been predicted by Stockmayer and Peebles.[16]

Comparison of High and Low Fractions.—The data in Table I show that relatively more L fraction is formed in dilute solution, corresponding to an over-all reaction of lower kinetic order than the 5/2-order for H fractions. This section will present further evidence from unsaturation measurements and from inhibitor effects that there are two distinct reactions involved in the formation of these fractions. Table III summarizes results on low molecular weight fractions. Distillation of the combined low fractions indicates that they consist of about 20 weight % dimer (28 mole %), and about 50% trimer. The dimer is largely saturated, and therefore cyclic, while the trimer and H fractions (not distilled) contain progressively more unsaturation. The L fractions made in the most dilute solutions may contain the most unsaturated material from chain transfer. Initiation by monoradicals and termination by either disproportionation or combination should yield polymer averaging one double bond per molecule. Transfer with monomer, and transfer with solvent without incorporation of solvent, produce one double bond per additional molecule. Disproportionation of biradicals also yields polymer averaging one double bond. The only apparent sources of saturated polymer are intramolecular coupling of biradicals or polymolecular reactions leading directly to cyclic compounds. These considerations suggest that most of the unsaturated material, including substantially all the high polymer, arises from chain reactions of monoradicals and that the saturated material arises from independent nonradical or biradical reactions, similar to the Diels–Alder reaction or the dimerizations of polyfluoroethylenes[25] and acrylonitrile.[26] In any event, the precipitation procedure used has only partially separated the two types of products.

TABLE III

PROPERTIES OF POLYSTYRENE FRACTIONS

Fraction	B.p., °C.	Wt., g.	Br_2 equiv.[a]	Mol. wt.	C=C per molecule
Undistilled fractions					
29–31L		1.85	572, 565	356	0.63
29–31H		5.58	1979, 1951	1549	.79
32–4L		1.51	606, 620	306	.50
32–4H		9.49	3675, 3629	2640	.72
2.80 g. combined low fractions distilled at 0.25 mm.[b]					
1	105–130	0.53	>2500	231	< 0.10[c] mobile oil
2	130–155	0.07			
3	155–190	1.38	564	338	.60 viscous oil
4	Residue	0.67	1215	548	.45 brown tar
16.36 g. low fractions (picric acid run) distilled at 0.3 mm.[d]					
A	90–115	4.15	1245, 1302[e]	235	0.18 mobile oil
B	115–137	0.65	697		
C	137–162	0.73	1290		
D	162–185	1.67	2780, 2619, 2676	330	.12 very viscous oil
E	Residue	8.54			Black tar

[a] Grams of sample required to absorb one mole of bromine. [b] Mostly remainders of fractions of runs 28–34, similar products from earlier runs also were included. [c] One analysis indicated a bromine equivalent of 2764; two others gave much higher values (no unsaturation). [d] 198 g. of styrene and 4 g. of picric acid were refluxed (*ca.* 145°) for 24 hours. Working up by the usual precipitation procedure gave 18.23 g. of L fraction and 36.34 g. of H fraction, both black and presumably containing 4 g. of picric acid residues. [e] Original bromine equivalent of light brown distillate was about 600 in a slow bromination. On several weeks standing, sample turned black and was redistilled. The light yellow distillate then had the indicated bromine equivalent, in a faster bromination.

These considerations account for the conclusion

---

(20) F. R. Mayo and W. B. Hardy, THIS JOURNAL, **74**, 911 (1952).

(21) (a) D. F. DeTar and H. J. Scheifele, Jr., *ibid.*, **73**, 1442 (1951); (b) D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 2094 (1952); (c) D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, **14**, 216 (1953).

(22) F. R. Mayo, *ibid.*, **2**, 372 (1947); M. T. Jaquis and M. Szwarc, *Nature*, **170**, 312 (1952).

(23) G. S. Hammond, J. T. Rudesill and F. J. Modic, THIS JOURNAL, **73**, 3929 (1951). The formation of equal proportions of tetraphenylmethane and benzoic acid may be represented by the sequence: $BzO\cdot + C_6H_6 \rightarrow BzOC_6H_6\cdot$; $BzOC_6H_6\cdot + (C_6H_6)_3C\cdot \rightarrow BzOH + (C_6H_5)_4C$. If the fast reaction with triphenylmethyl is not available, $BzOC_6H_6\cdot$ either loses CO_2 or usually decarboxylates as it reacts with $BzO\cdot$ to give biphenyl, benzoic acid, or phenyl benzoate. Direct reactions of $BzOC_6H_6\cdot$ and of $C_6H_5C_6H_6\cdot$ with benzoyl peroxide are not important in the presence of triphenylmethyl.

(24) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

(25) J. Harmon, U. S. Patent 2,404,374 (1946); J. R. Lacher, G. W. Tompkin and J. D. Park, THIS JOURNAL, **74**, 1693 (1952).

(26) E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949).

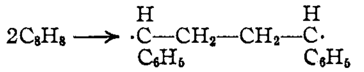
of Melville and Watson that there are two independent reactions between styrene and benzoquinone,[27] and suggest that the 2:1 reaction product found[27,28] results from a non-radical or biradical reaction. The recent work of Russell and Tobolsky[29] tends to support a brief existence of biradicals. They found that diphenylpicrylhydrazyl (a free radical and an inhibitor of polymerization) is consumed in pure styrene at a rate much faster than can be accounted for by the thermal initiation of high polymer chains. Further, this high rate of reaction with diphenylpicrylhydrazyl at 60° corresponds within a factor of two with that calculated if the L fraction of expt. A in Table I arises from biradicals.

In order to prepare more material of low molecular weight, styrene was polymerized in the presence of picric acid. This inhibitor strongly retarded formation of the H fraction without significantly affecting the rate of formation of L fraction. The L fraction contains more saturated products than are in the solvent runs. Comparison of infrared spectra of the dimer fractions 1 and A in Table III indicates that 1 may have come from partial oxidation of a mixture like A. Apparently, several months standing of some L fractions before distillation resulted in accumulation of some hydroxyl and carbonyl groups.

The saturated dimer is thought to be a mixture of *cis*- and *trans*-1,2-diphenylcyclobutanes and an effort will be made to establish its structure. The fraction A, by infrared spectra, differs from both of the dimers formed in the acid-catalyzed polymerization.[30] 1,3-Diphenyl-1-butene had absorption bands at 7.72, 9.92, 10.40 and 11.03µ, 1-phenyl-3-methylindane at 6.80, 7.55 and 9.13 µ, and fraction A at 8.10, 11.31, 12.61 and 12.82 µ, with no duplication of the absorption bands cited.

Mechanism of Thermal Chain Initiation.—Although a decision cannot be made between non-radical and biradical mechanisms for the formation of saturated polymer in the L fractions, this section will show that either biradicals (if any) are not important precursors in the formation of high polymer or else they are abnormally reactive in chain transfer. A termolecular reaction of styrene to give two monoradicals is proposed for thermal initiation. As a satisfactory approximation in the present discussion, the L fractions are assumed to contain only products of the non-radical or biradical reaction, and the H fractions are assumed to contain only products of a monoradical chain polymerization reaction.

On the basis that the over-all rate of thermal polymerization is second order, and from energy considerations, thermal initiation has previously been assumed to be a second-order reaction of two styrene molecules to give a biradical[31,2a,b]



$$2C_8H_8 \longrightarrow \cdot\underset{C_6H_5}{\overset{H}{C}}-CH_2-CH_2-\underset{C_6H_5}{\overset{H}{C}}\cdot \qquad (13)$$

However, Zimm and Bragg[32] have recently shown, from Matheson's rate constants,[9] that styrene biradicals cannot grow very large without self-destruction, and they have proposed that the necessary monoradicals arise from biradicals by chain transfer. In Table I, expt. A at 60° and expt. 20 at 155° now show that not enough low polymer is formed *in the absence of solvent* to account for the formation of high polymer. If the number of moles of low polymer found corresponds to the number of moles of biradicals generated, (7×10^{-5} at 60°, 1.1×10^{-4} at 155°), then even in ten propagation steps per radical pair only $10C_m$ (0.0006 at 60°, 0.004 at 155°) of these will be converted to monoradicals by transfer with the monomer, much less than the number of moles of high polymer formed (2.54×10^{-6} at 60°, 1.34×10^{-5} at 155°, half of which came from transfer with the monomer during prolonged growth of monoradicals). Hence biradicals of the same activity in chain transfer as polystyrene monoradicals are inadequate as a source of monoradicals in the absence of solvents, but origin of some monoradicals in this manner cannot be entirely excluded.

The following considerations demonstrate that biradicals (if any) have too short a life *in dilute solution* to contribute to the formation of high polymer. At 155°, with $0.1M$ styrene in bromobenzene, the third-order initiation is exceedingly slow, $2.3 \times 10^{-12} \times 2$ monoradicals in moles/l./sec. by eq. 5. This low rate of initiation is partly offset by the longer kinetic chain lengths in dilute solution, 17600 (reciprocal of last term in eq. 9, 10) per radical pair at $0.1M$ styrene, as compared with 2000 at $7.5M$. These relations are consistent with all the rate and molecular weight data on high polymers in this paper. From expt. 32–34, the rate of formation of low polymer at 155° corresponds to 1.0×10^{-8} mole of monomer/l./sec. at $0.1M$ styrene (half as much by eq. 7). Since this polymer averages about three styrene units, the rate of the initiation reaction producing it can be taken as 3×10^{-9} mole/l./sec. If this were the rate of formation of biradicals, and if each were to have the normal ratio of transfer and propagation constants, then for one propagation step of either end, the fraction transferring with the monomer would be C_m, 4×10^{-4}, and the fraction transferring with the solvent at a bromobenzene:styrene ratio of 91 would be $91 \times 3 \times 10^{-4}$ or 273×10^{-4}. The rate of formation of monoradicals for one propagation step of the biradicals would then be the rate of formation of the latter, 3×10^{-9}, times the fraction transferring, $(4 + 273) \times 10^{-4}$ times 2, or 2×10^{-10} mole/l./sec. This number is so large compared with the rate of third order direct monoradical initiation estimated first above, 4.6×10^{-12}, that we must conclude that if any biradicals are formed, fewer than 1% of them last long enough to grow even one step. If they did survive that long, formation of monoradicals by the accompanying transfer reactions would greatly

---

(27) H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948). Some of their conclusions concerning quinone inhibition of thermal and peroxide initiated polymerizations have not been substantiated.[10]

(28) W. Kern and K. Feuerstein, *J. prakt. Chem.*, **158**, 186 (1951).

(29) K. E. Russell and A. V. Tobolsky, This Journal, **75**, 5052 (1953).

(30) P. E. Spoerri and M. J. Rosen, *ibid.*, **72**, 4918 (1950).

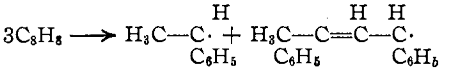
(31) P. J. Flory, *ibid.*, **59**, 241 (1937).

(32) B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952).

exceed that from observed third-order initiation. Actually, k_2 for fraction L is based on products including both saturated and unsaturated polymers of two, three and more units. The rate of formation of any single product is only a fraction of the total and we cannot be sure of the order of any one reaction. Although the ability of any one of the possible biradical reactions to transfer is less than in the example, it will still be too large to resolve the discrepancy in dilute solution.

Further, the similarity in rates of polymerization of styrene in a wide variety of solvents[2c,f,g] is difficult to account for if transfer of biradicals is important in monoradical initiation. These conclusions are supported by the results of Tobolsky and co-workers[33] who have sought evidence for biradicals in thermal and photopolymerizations and have found none. The present work, together with that of Zimm and Bragg,[32] suggests that further searches, even with biradical initiators, will probably also be unsuccessful.

The third-order thermal initiation now provides a means of generating pairs of monoradicals within the observed activation energy for initiation of 29 kcal./mole. If three monomer units react to give two monoradicals, *e.g.*



$$3C_8H_8 \longrightarrow H_3C{-}\overset{H}{\underset{C_6H_5}{C}}\cdot + H_3C{-}\underset{C_6H_5}{C}{=}\overset{H}{C}{-}\overset{H}{\underset{C_6H_5}{C}}\cdot \qquad (14)$$

the number of double bonds lost and of single bonds formed is the same as in reaction 13, which has previously seemed reasonable.[31,34] The sole basis for preferring the above structures of the monoradicals is conjugation and resonance stabilization. The termolecular initiation mechanism probably involves all three styrene units in a single activated complex: if a biradical were formed reversibly and were stabilized by adding to styrene,[31] the result would still be a biradical, which cannot account for formation of high polymer. From kinetics, the termolecular reaction is probably very efficient in starting monoradical chains; at least its efficiency must be independent of monomer concentration.

The best alternative to the above initiation mechanism is the formation of a biradical by process 13, followed by a very inefficient transfer reaction with monomer to give two monoradicals. Since it has been shown that ordinary chain transfer is insufficient to account for initiation by this route in undiluted styrene, a postulate of an abnormally high tendency for chain transfer between biradicals and monomer (but not with solvent) to give two monoradicals (possibly in a concerted reaction) is required. The efficiency of initiation of monoradicals must be very low because of the high molar ratio of low to high polymer.[35] In undiluted styrene, the biradicals may survive long enough to react with reactive inhibitors, and even for some of them to add a monomer unit, but in 0.1*M* solution, few, if any, can survive long enough to add even one styrene unit.

The Breitenbach Experiment.—Finally, some comment seems appropriate on the original experiment of Breitenbach[6a] with 0.1*M* styrene in chlorobenzene at 153°, where his product was a chlorine-free material of molecular weight 410. Since his own more recent experiments[6b] point to much higher molecular weights, the present work suggests that his solvent contained an inhibitor and that he may have obtained only the non-radical or biradical polymerization, but it supports his discovery that low molecular weight polymers made in chlorobenzene were halogen-free, in contrast to low polymers made in carbon tetrachloride, which contained considerable chlorine.[36] While his view that the reduction in molecular weight without incorporation of solvent is a dilution effect[6b,c] which does not show up in the kinetics cannot be excluded, the present paper presents a close correlation of both rates and molecular weights over a wide concentration range on the basis of third order initiation and of chain transfer without incorporation of solvent.

Acknowledgment.—The author is indebted to many of his associates for assistance in this research: to Mr. E. M. Hadsell for many distillations of bromobenzene, to Mr. L. B. Bronk for some bromine analyses and supervision of much of the analytical work, to Mrs. Patricia Morrison for crysocopic molecular weights and viscosity determinations, to Mrs. D. K. Ladd for many precipitations, distillations and determinations of unsaturation, to Dr. R. S. McDonald and Mr. C. A. Hirt for infrared spectra, and to Drs. B. H. Zimm and J. K. Bragg for many helpful discussions.

SCHENECTADY, N. Y.

---

(33) D. H. Johnson and A. V. Tobolsky, THIS JOURNAL, **74**, 938 (1952); B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **8**, 529 (1952).

(34) Taking 80 and 145 kcal. as the C—C and C=C bond energies (K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948)), three single bonds are formed and two double bonds lost in either reaction. The difference, 50 kcal., can be offset by twice the resonance stabilization of the benzyl radical (15–20 kcal./mole, M. Szwarc, *Proc. Roy. Soc.* (*London*), **207**, 5 (1951)), and also, in the termolecular reaction, by conjugation of the free radical, double bond and phenyl groups. It should be noted that styrene, where resonance stabilization is most obvious, is most conspicuous for exhibiting a reproducible thermal polymerization.

(35) The complex dependence on the monomer concentration of the rate of the benzoyl peroxide initiated polymerization of styrene in toluene, later observed in benzene,[2f] led to the postulation of a cage effect by M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945). Application of this treatment to present data on thermal polymerization led to no entirely satisfactory correlation in plots of $[\text{monomer}]^n/(\text{rate of polymerization})^2$, where n = 4–7. To the extent that qualitative conclusions can be drawn from the plots, the over-all reaction is $^5/_2$ order in bromobenzene solution and the rate for expt. 20 is unexpectedly low in comparison with the other rates. The $^5/_2$-order reaction may result either from an efficient process like 14 or a very inefficient process like 13 followed by chain transfer. In the latter case, the k_{3i} calculated in eq. 5 is a complex constant.

(36) J. W. Breitenbach, A. Springer and E. Abrahamczik, *Öesterr. Chem. Z.*, **41**, 182 (1938); J. W. Breitenbach and A. Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).