definition would restrict true cation exchange resins to those which contain only completely dissociated acidic groups, *i. e.*, strong acid resins.

BROOKLYN, N. Y. RECEIVED DECEMBER 27, 1947

[CONTRIBUTION NO. 75 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene. II. The Reaction of Styrene with Carbon Tetrachloride[1]

BY R. A. GREGG AND FRANK R. MAYO

Using literature data on the uncatalyzed polymerization of styrene, a previous paper[2] from this Laboratory showed that the effects of solvents in reducing the molecular weight of polymerizing styrene could be correlated on the basis that the growing polymer radical captures an atom from the solvent molecule, resulting in a radical which starts a new chain[3] and in the incorporation of solvent in the polymer. Since these relations promised to be useful in making quantitative comparisons of the reactivities of solvents toward free radicals, a thorough test of the equations and concepts on the styrene–carbon tetrachloride system was begun. The present paper considers both the uncatalyzed and peroxide-catalyzed polymerization of styrene at 60–132° to give products averaging more than thirty styrene units per polymer molecule, or per incorporated carbon tetrachloride molecule. A succeeding paper[4] will consider formation of products averaging as low as two styrene units per carbon tetrachloride residue.

Experimental

Purification of Materials.—Dow styrene was freed from inhibitor by vacuum distillation and the middle fractions were partially crystallized by stirring in a Dry Ice-bath. The process was repeated from six to eight times until the freezing point became constant. The recrystallized material was distilled under nitrogen: b. p. 44.9–50° at 18 mm.; n^{20}_{D} 1.5465; f. p. −30.7° ± 0.1°. The styrene was stored in sealed, evacuated tubes in Dry Ice.

Reagent grade carbon tetrachloride was stirred with concentrated sulfuric acid and then with potassium hydroxide solution, washed with water, and dried over calcium chloride. It was distilled from paraffin wax[5] through a 1-meter helices-packed column: b. p. 76.8° at 760 mm.; n^{20}_{D} 1.4605.

Benzoyl peroxide was twice dissolved in cold chloroform and precipitated by pouring into cold methanol, collected on a sintered glass filter, and dried under vacuum at room temperature. It liberated 100.0–100.4% of the theoretical quantity of iodine from potassium iodide in glacial acetic acid.[6]

Preparation of Polystyrene Samples.—Weighed amounts of carbon tetrachloride and styrene (and benzoyl peroxide, when used) were placed in a flamed Pyrex tube equipped with a standard taper joint. The tube was attached to the vacuum line and the sample was frozen in liquid nitrogen. The tube was then evacuated and the sample was degassed twice by thawing and refreezing. The tube was then sealed at a pressure of 10^{-5} mm. Check experiments in which both the solvent and the styrene were distilled under high vacuum into the reaction tube showed no difference, even with large volumes of other solvents. The polymerizations were carried out in thermostats at 60 ± 0.05°, 100 ± 0.1°, and 132 ± 1°, and held to about ten per cent. conversion.

The polymer was precipitated with methanol and redissolved in twenty-five to fifty times its weight of benzene. This solution was then treated with three to five times its volume of methanol. An additional solution and precipitation was used for many of the samples whose molecular weights were determined osmometrically. The decanted precipitating medium was usually centrifuged to obtain any suspended polymer. The polymer was dissolved in benzene; the solution was frozen in Dry Ice, and the benzene was removed by sublimation.[7]

The above procedure results in loss of some of the very low molecular weight polystyrene; where the average molecular weight of the polymer was low, some of the precipitating solutions were rapidly concentrated by distillation *in vacuo* and the residue was dissolved in benzene and added to the main portion of the polymer. This procedure permits distillation of monomer from a *small* amount of *low* molecular weight polymer instead of from the whole polymer and gave products, marked in Table I, with appreciably lower average degrees of polymerization.

Determination of Number Average Molecular Weights from Osmotic Pressure.—These determinations were made by Drs. R. H. Ewart, H. C. Tingey and M. Wales.[8] The osmotic pressures were measured either in glass[9] or metal osmometers[10] with cellophane membranes and at three or more concentrations. Either butanone or benzene was used as the solvent, with identical end results.

Viscosity Determinations.—Solution viscosities were determined in benzene at 30°, using Fenske viscometers with 80–120 second flow times and neglecting kinetic energy corrections. Such corrections would give an increase of about 5% in intrinsic viscosities but would not affect the present molecular weight estimates from viscosity data. Where the molecular weight was determined independently, the intrinsic viscosity,[11] $[\eta]$, was obtained from specific viscosities at three or more polymer concentrations. Otherwise, the intrinsic viscosity was obtained from the specific viscosity of a single solution, measured in two

---

[1] This paper was presented before the Polymer Forum at the Atlantic City Meeting of the American Chemical Society, April 10, 1946.

[2] Mayo, THIS JOURNAL, **65**, 2324 (1943).

[3] Essentially the same development has been made independently by Hulburt, Harman, Tobolsky, and Eyring, *Ann. N. Y., Acad. Sci.*, **44**, 371 (1943), and by Medvedev, Koritskaya and Alekseeva, *J. Phys. Chem. U. S. S. R.*, **17**, 391 (1943).

[4] Mayo, paper submitted to THIS JOURNAL.

[5] Weissberger and Proskauer, "Organic Solvents," Oxford University Press, 1935, p. 156.

[6] Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).

[7] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1943).

[8] Ewart and Tingey, *Abstracts of Papers*, 111th Meeting American Chemical Society, April, 1947, p. 4Q.

[9] French and Ewart, *Ind. Eng. Chem., Anal. Ed.*, **19**, 165 (1947).

[10] Flory, THIS JOURNAL, **65**, 372 (1943).

[11] Kraemer and Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

TABLE I

THERMAL POLYMERIZATION OF STYRENE IN CARBON TETRACHLORIDE

$\frac{[CCl_4]^{a}}{[Styrene]}$	Time, hr.	Yield, %	kb × 10^4	$[\eta]$	No. av. mol. wt. × 10^{-3}		Analyses, % Cl	$1/\overline{P}$ × 10^5		C × 10^5	
					(osmotic)	(Cl)^{c}		($[\eta]$)^{d}	(Cl)^{e}	($[\eta]$)^{f}	(Cl)^{g}
Experiments at 60°											
0.000			1.1^{j}	3.43^{k}				10.1($1/\overline{P}_0$)			
.00291	85	6.8	1.00	2.94				12.6		830	
.00614	85	6.9	1.06	2.46	610 ± 60			16.1		950	
.0214	95	7.7	1.16	1.90	510 ± 40			23.1		1010	
.0186	115.4	9.14	1.02	1.70				27.1		870	
.0267	93	7.7	1.01	1.39	290 ± 40			35.9		920	
.0393	115.4	11.68	1.35	1.10				49.8		950	
.0413	112.2	8.8	1.00	1.06	237 ± 15	159	0.075	52.4	66	975	1270
.0704	112.2	9.1	1.08	0.826	131 ± 5			74.8		880	
.074	162.5	16.1	1.45	.69	125			95.7		1070	
.1000	85	5.4	0.78	.64	107 ± 10			106		930	
.1026	212	19.4	1.42	.60				117		940	
.1615	85	7.9	1.29	.494	82 ± 5			153		850	
.1643		6.28	0.89	.486		63	.212	156	167	860	920
.1958		5.22	0.60	.35		42	.339	247	260	1180	1250
.2595	85	9.0	1.63	.356	50^{m}			242		850	
.3045	113.5	9.08	1.32	.314		30.3	.41	289	314		952
.3645	160	6.2	0.76	.26	< 50	27.9	.480	376	375		967
.4515	160	10.5	1.19	.25		26.5	.521	397	395		810
.471	159.2	11.9	1.38	.237		25.5	.541	429	410		798
.682	187.7	11.5	1.23	.196		18.3	.760	563	573		778
.853	185	7.23	0.86			13.7	1.02		769		854
.931	187.7	9.82	1.23	.168		14.8	0.94	696	709		712
.940	92.3	11.7	1.84	.155		14.4	0.967	780	730		721
1.000	192	5.12				13.4	1.04		784		752
1.052	285	12.25^{h}	0.94			10.5	1.34		1002		885
1.051	285	12.25^{h}	0.94			10.7	1.32		984		879
1.181	92.3	8.8	2.49	.142		12.7	1.10	890	830		657
2.043	252	2.68	0.36			6.87	2.05		1550		742
Experiments at 100°											
0.000	4.1	9.17	28.5^{l}	1.81^{k}				24.8($1/\overline{P}_0$)			
.00582	4.1	10.81	34.6	1.38				36.3		1860	
.0124	4.0	10.31	35.3	1.14	216	199	0.037	47.3	52	1710	2070
.0222	4.3	9.95	32.3	0.876	159	142	.066	68.4	74	1860	2080
.02643	5.3	10.90	27.3	.82				75.2		1810	
.0416	4.3	10.27	31.6	.628	105	80	.143	109	130	1930	2400
.0496	4.0	9.37	30.5	.573	93	82	.139	124	127	1910	1960
.0892	4.3	9.20	30.0	.428	58	48	.26	187	217	1730	2050
.194	4.3	8.32	27.5	.261		29.2	.45	374	358		1640
.3157	4.3	7.37	27.5	.204		18.5	.735	531	570		1660
.4943	6.6	8.90	30.8	.158		13.6	1.01	758	776		1450
.676	7.5	10.59	29.3	.133		10.8	1.28	969	978		1330
.683	8.0	4.70	13.7			7.95	1.75		1335		1870
.890	8.0	7.39^{h}	20.6			6.90	2.02		1541		1640
1.023	12.0	13.1	27.1			6.06	2.30		1760		1630
1.228	11.0	8.08	15.9	.084		6.55	2.13	1860	1626		1248
1.980	16.6	*ca.* 10^{h}				3.45	4.07		3155		1500
2.00	16.8	9.81	20.2			3.60	3.9		3010		1420
2.043	15.8	8.16	17.9			3.65	3.86		2980		1390
3.05	23.2	8.08	15.9			2.56	5.50		4300		1340
0.211^{i}	45.4	10.33	20.6	.233				438		1860	
Experiments at 132°											
0.000	0.83	18.2	308^{l}	$.99^{k}$	171 ± 2.6		0.00	57.6($1/\overline{P}_0$)			
.0341	.83	19.0	331	.46		57	.172	169	185	2950	3370
.0713	.83	17.2	304	.31		33.5	.345	294	311		3260
.100	.9	19.55	344			29	.41		360		2730
.150	.9	15.57	269			19.4	.655		541		2980
.200	.9	16.25	290			15.0	.87		701		2970

[a] Initial molar solvent : monomer ratios. [b] Over-all second order rate constant in liters mole^{-1} hour^{-1}. [c] Equation (7). [d] Equations (2) and (8). [e] Equations (5–6). [f] Equation (3). [g] Equation (4). [h] Precipitating media concentrated to recover dissolved polymer. [i] Five volumes of benzene used as diluent for styrene–carbon tetrachloride mixture. [j] Average value from six experiments. [k] Averaged value, maximum deviation 0.05. [l] Single representative experiment. [m] For weight average and Z-average molecular weights, see Wales, Bender, Williams and Ewart, *J. Chem. Phys.*, **14**, 353 (1946).

different viscometers, and the equation

$$[\eta] = \frac{\sqrt{1 + 1.5\eta_{sp}} - 1}{0.75C_v} \qquad (1)$$

where C_v is the grams of polymer per 100 cc. of solution at the temperature of the viscosity measurement.

Chlorine Determinations (by Dr. O. W. Lundstedt and Mr. G. S. Mills).—For the determination of very small proportions of chlorine, the method of Shriner[12] was modified. A 20 mm. i. d., 80-cm. Vycor tube was heated in a furnace to about 800°. The tube had a 15 cm. section of crushed platinum foil in the hottest portion of the furnace and the remainder of the tube was packed with crushed Vycor interspersed with 50-mesh platinum disks. Oxygen, at a rate of 20 cc. per minute, was used to burn the sample which was heated by a mechanically-advanced auxiliary furnace. The products were absorbed in 5 ml. of 3% hydrogen peroxide and 1 ml. (20 mg.) of sodium acetate solution contained in a six bulb Will-Varrentrapp type absorber. The sample size was such that 2–10 ml. of silver nitrate were required. The halogen was titrated with 0.01 *N* silver nitrate in 50% acetone solution with dichlorofluorescein indicator according to the recommendations of Bullock and Kirk.[13] Blanks were negligible and analysis of a known sample agreed with the theoretical within two parts per thousand.

Results and Discussion

The Relation between Intrinsic Viscosity and Number Average Molecular Weight for Unfractionated Polystyrene.—In order to permit molecular weight determinations on unfractionated polystyrenes from viscosity measurements, the relation between number average molecular weight, $\overline{M}_n$, and intrinsic viscosity, $[\eta]$, was determined. Molecular weights of polystyrenes by osmotic pressure determinations in the molecular weight range 50,000–600,000 and by chlorine analyses in the range 10,000–200,000 are compared with intrinsic viscosities in Table I and Fig. 1. The figure shows that, within experimental error, over the range 10,000–600,000

$$\overline{M}_n = 184{,}000\ [\eta]^{1.40} \qquad (2)$$

and this relation was used to calculate number average molecular weights in all experiments where viscosities were determined.[14] Equation (2) is applicable only to polystyrenes prepared at low conversions where the molecular weight distribution is uncomplicated by changing solvent–monomer ratio or branching reactions.[15] The relation is apparently independent of the chain transfer solvent[8,14] and temperature.[16]

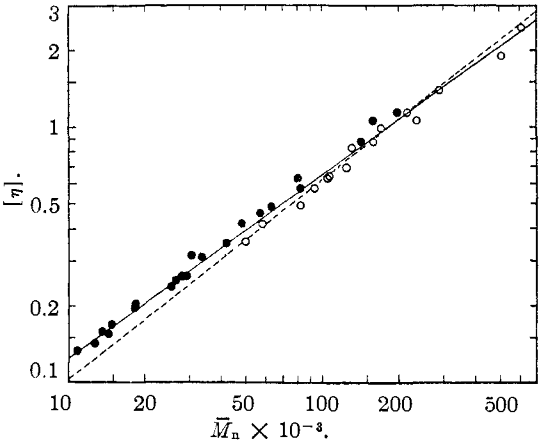

Fig. 1.—Relation between intrinsic viscosity, $[\eta]$, and number average molecular weight, $\overline{M}_n$, for unfractionated polystyrenes prepared at 60°, 100°, and 132° in presence of carbon tetrachloride: $\overline{M}_n$ by osmotic pressure, ○, by chlorine analysis, ●. Solid line corresponds to Equation (2), broken line to older equation.[14]

Transfer Constant of Carbon Tetrachloride in the Thermal Polymerization of Styrene.—Table I summarizes results on the uncatalyzed polymerization of styrene in carbon tetrachloride. The reactions involved were discussed previously[2] and it was shown that

$$1/\overline{P} = C[\mathrm{S}]/[\mathrm{M}] + 1/\overline{P}_0 \qquad (3)$$

---

(12) Shriner, "Quantitative Analysis of Organic Compounds," Edwards Bros., Inc., Ann Arbor, Mich., 1944, pp. 26–27.

(13) Bullock and Kirk, *Ind. Eng. Chem., Anal. Ed.*, **7**, 178 (1935).

(14) A large number of osmotic determinations on polystyrenes of molecular weight 50,000–600,000, prepared in various other solvents, without catalysts at three temperatures and with benzoyl peroxide at 60°, had indicated the relation[8]

$$\overline{M}_n = 184{,}000\ [\eta]^{1.277}$$

used previously by Gregg and Mayo, *Trans. Faraday Soc.*, **43B**, in press (1947). For molecular weights above 50,000, the two equations give substantially the same results.

(15) Equation 2 is based upon polystyrenes with a distribution function (assumed to be) governed by termination through chain transfer and disproportionation and with the termination steps independent of chain length. If polystyrene chains in the absence of solvent terminate by combination of radicals, then $\overline{P}_0$ values calculated from intrinsic viscosities and Equation 2 should be too low by about 20%. However, osmotic determinations on polymers from pure styrene at 100 and 132° give $\overline{P}_0$ values agreeing with those calculated from Equation (2). For 60° polymers, osmotic determination of $\overline{P}_0$ is impractical, but plots of $1/\overline{P}$ (from osmotic determinations) against solvent:monomer ratio extrapolate to the $1/\overline{P}_0$ value calculated from intrinsic viscosity. The data thus reveal no different distribution of molecular weights in the absence of solvent.

(16) Similar equations have been proposed for polystyrene fractions and an effect of temperature of preparation of the polymer has been reported, Alfrey, Bartovics and Mark, THIS JOURNAL, **65**, 2319 (1943).

where $\overline{P}$ and $\overline{P}_0$ are the degrees of polymerization of styrene, in the presence and absence of solvent, respectively, at solvent and monomer concentrations [S] and [M], and where C, the transfer constant, is the ratio of the rate constants for chain transfer and chain growth for all polystyrene radicals. An effort was made to hold reaction of the styrene to 10% or less. The small variation in over-all second order rate constant with solvent: monomer ratio shows that the thermal reaction is not seriously complicated by traces of catalysts and justifies the assumption in deriving Equation (3) that the rate constants for chain initiation, growth, and termination do not change significantly with solvent or chain length.

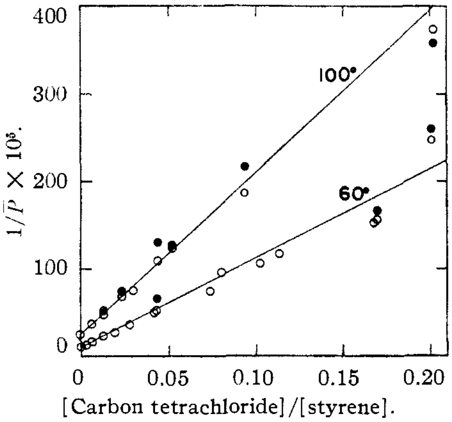

Fig. 2.—Thermal polymerization of styrene in carbon tetrachloride: $1/\overline{P}$ from intrinsic viscosity, ○; from chlorine analysis, ●.

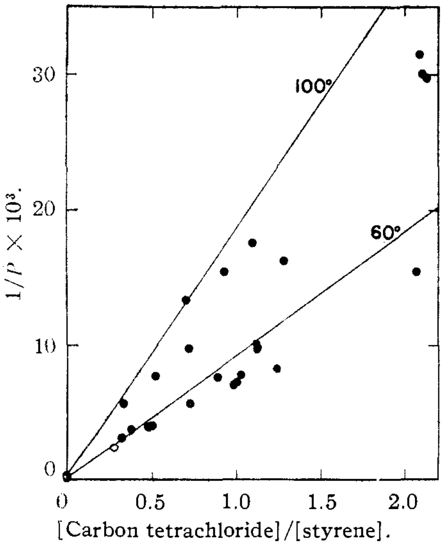

Fig. 3.—Thermal polymerization of styrene in carbon tetrachloride: $1/\overline{P}$ from intrinsic viscosity, ○; from chlorine analysis, ●.

Except for low degrees of polymerization, where the proportion of monomer consumed in starting polymer chains cannot be neglected[4]

$$C[\mathrm{S}]/[\mathrm{M}] = \mathrm{d}[\mathrm{S}]/\mathrm{d}[\mathrm{M}] \tag{4}$$

where d[S]/d[M] is the molar ratio of solvent to monomer in the polymer being formed. The average degree of polymerization and number average molecular weight, $\overline{M}_n$, in Table I are calculated from chlorine analyses by the relations

$$\mathrm{d}[\mathrm{S}]/\mathrm{d}[\mathrm{M}] = 104.14/[(14183/\%\ \mathrm{Cl\ in\ polymer}) - 153.84] \tag{5}$$

$$1/\overline{P} = \mathrm{d}[\mathrm{S}]/\mathrm{d}[\mathrm{M}] + 1/\overline{P}_0 \tag{6}$$

$$\overline{M}_n = 104.14\ \overline{P}(1 + 153.84\ \mathrm{d}[\mathrm{S}]/104.14\ \mathrm{d}[\mathrm{M}]) = 104.14\ \overline{\mathrm{P}}/(1 - 0.01085\%\ \mathrm{Cl}) \tag{7}$$

$\overline{M}_n$ is also determined from intrinsic viscosity by Equation (2); then

$$1/\overline{\mathrm{P}} = (104.14-153.84/\overline{P}_0)/(\overline{M}_n - 153.84) \backsimeq 104/(\overline{M}_n - 154) \tag{8}$$

The transfer constant, C, is calculated from Equations (3) or (4).

Since, in each experiment, the styrene concentration decreases appreciably while the carbon tetrachloride concentration does not, *average* solvent:monomer ratios have been used in all calculations and plots. Calculations of transfer constants in Table I are based on all chlorine analyses and on intrinsic viscosities above 0.35 (where they have been standardized against osmotic molecular weights) and in Figs. 2 and 3 the same data for 60 and 120° runs have been plotted for graphical determination of transfer constants. The lines in Figs. 2 and 3 are based on experiments with solvent:monomer ratios below 0.4 and other experiments where low molecular weight material was recovered after polymer precipitation. The slopes of the lines are the transfer constants for carbon tetrachloride with styrene at 60° and 100°, 0.0092 (±0.0010) and 0.0185 (±0.0022), respectively, the experimental error being taken as the standard deviation of the transfer constants in Table I for those experiments on which the lines were based. The two 1:1 experiments at 60° where low molecular weight material was recovered fall slightly below the line only because of the failure of Equation (3) to apply to low degrees of polymerization and the failure of the shortest radicals to transfer normally,[4] but only part of the deviation of the best 100° experiments can be ascribed to these causes. Almost all other experiments at 60° and 100° at solvent:monomer ratios above 0.4 show the effects of loss of low molecular weight material in precipitating polymer. The linear relation between solvent:monomer ratio and $1/\overline{P}$ is taken as proof that the transfer constant, the ratio of the rate constants for chain transfer and chain growth, is substantially constant for radicals averaging 100–10000 styrene units.

The transfer constant at 132° is taken as the average of the six values in Table I, 0.0304 (±0.0023). From the values of the transfer constant at 60, 100, and 132°, the activation energy for chain transfer is found to be about 4.5 kcal./mole higher than for chain growth and the frequency factor for transfer is then about eight times as large as for growth.

The reaction mixture in the last listed experiment at 100° was diluted with five volumes of benzene, which, in comparison with carbon tetrachloride, is substantially inert in chain transfer.[2,14] Since the rate of reaction and the molecular weight of the product were entirely consistent with the other experiments, the use of an inert diluent is justified in the experiments in Table II.

Transfer Constants from Peroxide Initiated Polymerizations.—In order to extend quantitative work on chain transfer to other monomers and to very low styrene concentrations, where uncatalyzed rates are very small or difficultly reproducible, the benzoyl peroxide–catalyzed polymerization of styrene was investigated. The relation between monomer and peroxide concentration and rate and degree of polymerization seems well established[17,18] and has recently been interpreted by Matheson[19] in this Laboratory. Matheson's equations and previous methods[2] have been used to derive Equation (9)

$$1/\overline{P} = C\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2(k_{\mathrm{a}}k_3\ [\mathrm{peroxide}])^{1/2}}{k_2[\mathrm{M}]}\left(\frac{k_{\mathrm{c}}[\mathrm{M}]}{k_{\mathrm{b}} + k_{\mathrm{c}}[\mathrm{M}]}\right)^{1/2} \qquad (9)$$

Here k_{a}, k_{b} and k_{c} are, respectively, the rate constants for the primary dissociation of peroxide into radicals, the first order recombination of radicals from the peroxide, and the reaction of these radicals with styrene; k_2 and k_3 are the rate constants for chain growth and termination. Uncatalyzed initiation is neglected and the final factor is the fraction of peroxide radicals which initiate chains. This development assumes that the rate constants concerned are independent of the composition of the polymerizing system, a condition which is met in Table II, as shown by the over-all rates. The condition may not be met when the decomposition of the peroxide is affected by the solvent.[20] This equation may be applied for low conversions under either of two sets of conditions. If solvent and monomer concentration are kept constant while the peroxide concentration is varied, C is obtained from the intercept of the line formed by plotting $1/\overline{P}$ *vs.* [peroxide]$^{1/2}$. This method has thus far given poor results partly because of the extrapolation involved and the necessity for keeping conversions low and equal.

TABLE II

PEROXIDE-INITIATED POLYMERIZATION OF STYRENE AT 60° AT VARIOUS CONCENTRATIONS OF CARBON TETRACHLORIDE[a]

$[\mathrm{CCl_4}]$ Styrene	Conversion,[b] %	Rate %/hr./[peroxide]$^{1/2}$	[η]	$1/\overline{P}$ × 10^5[c]
0.0256	7.31	15.8	1.24	42
.0513	7.30	15.8	0.90	66
.0769	7.22	15.6	.72	90
.1026	7.35	15.9	.61	113
.1535	6.86	14.9	.40	205
.2053	6.79	14.7	.36	228
.2566	6.96	15.1	.35	247

[a] The carbon tetrachloride was added to 23.0-ml. aliquots of a solution of 0.0261 g. of benzoyl peroxide in 157.9 g. of styrene. Benzene was added until the volume of each run was 28.0 ml. [Styrene] = 7.14 moles/liter; $[\mathrm{Bz_2O_2}]$ 0.000507 mole/l. [b] In twenty and one-half hours. [c] Calculated from Equations (2) and (8).

If the concentrations of both monomer and peroxide are held constant, C is the slope of the line formed by plotting $1/\overline{P}$ *vs.* [S]/[M]. Table II and Fig. 4 illustrate this method, benzene being used as an inert diluent. The slope of the line (determined by the least squares method, assuming no error in [S]/[M]) and the transfer constant are 0.0093, in excellent agreement with the value obtained in thermal polymerization. This method may be applied to monomers or solvents which cannot be freed of peroxides and to monomers which themselves undergo chain transfer.

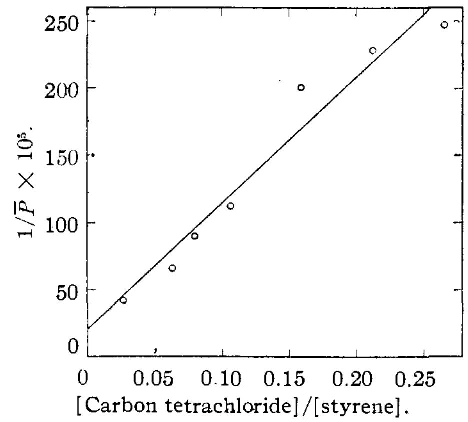

Fig. 4.—Benzoyl peroxide catalyzed polymerization of styrene in presence of carbon tetrachloride at 60°.

Summary

The polymerization of styrene in carbon tetrachloride has been studied over the temperature range 60–132°, over a range of solvent:monomer ratios from 0.003 to 3, and in the presence and absence of benzoyl peroxide as catalyst. Equations are presented which account for the average molecular weights (2500 to 1,000,000) of the products obtained. At 60°, the rate constant for the reaction of a growing polymer radical with carbon tetrachloride is 0.0092 times as large as the rate constant for addition of the radical to styrene. The temperature coefficient of this ratio shows that the chain transfer reaction has both a higher activation energy and a higher frequency factor. The constancy of this ratio and of the over-all rate con-

---

[17] Schulz and Husemann, *Z. physik. Chem.*, **39A**, 246 (1941); Schulz and Blaschke, *ibid.*, **51A**, 75 (1942).

[18] Josefowitz and Mark, *Polymer Bull.*, **1**, 140 (1945).

[19] Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[20] Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946); Cass, *ibid.*, **68**, 1976 (1946).

stant for polymerization indicate that the reactions of the growing polymer radical are independent of average chain length over the range 100 to 10,000 styrene units. The results establish the validity of a simple and accurate method for comparing the reactivities of solvents in general with the free radicals which occur in polymerizing systems.

Number average molecular weights of the products of thermal polymerizations of styrene at low conversions have been determined by osmotic pressure measurements and by chlorine analyses; they bear a simple relation to the intrinsic viscosities of the unfractionated polymers.

PASSAIC, N. J. RECEIVED JULY 19, 1947

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. IV. Vinylthiophenes[1,2]

BY G. BRYANT BACHMAN AND LOWELL V. HEISEY

The desirable polymerization and copolymerization characteristics of the chlorinated styrenes[3] and alpha-methylstyrenes[2b] have suggested studying their analogs in the thiophene series. We have synthesized a representative group of compounds with one, two or three chlorine or bromine atoms and an alpha- or beta-vinyl or isopropenyl group substituted on the thiophene nucleus. These compounds have been found to polymerize and copolymerize similarly to the corresponding benzene compounds, the rates increasing with the number of chlorine atoms present on each thiophene nucleus. The polymers were all somewhat colored, however, in spite of careful purification of the monomers. This seems to be inherent in the alpha-halothiophenes themselves. Even 2-chlorothiophene, which is color stable in stoppered tubes at 70° for days, colors within a few hours at this temperature in the presence of peroxides.

The preparation of vinylthiophenes is a problem very similar in nature to that of preparing vinylbenzenes except that the thiophene nucleus is more reactive, less stable, and subject to different rules of orientation than the benzene nucleus. We have been especially interested in observing the results of exchange metallation in the thiophene series. Either an alpha-hydrogen or an alpha-halogen may be replaced by lithium when treated with alkyllithium compounds. Thus 2-chloro-, 2,5-dichloro- and 2,3,4,5-tetrachlorothiophenes gave the corresponding metallo-derivatives with lithium in the 2-position and chlorine in the 5-, 5- and 3,4,5-positions, respectively. Magnesium reacted with 2,5-dibromothiophene normally, but with 2-bromo-5-chloro- and with 2,3,4,5-tetrachlorothiophenes it reacted well only in the presence of a co-halide (ethyl bromide). These lithium reagents and the corresponding Grignard reagents gave alcohols (Table I) with acetaldehyde, propionaldehyde, or acetone which were readily dehydrated to the desired vinylthiophenes (Table II). Some of the tertiary alcohols dehydrated spontaneously during isolation. Other vinylthiophenes were prepared from the corresponding methyl thienyl ketones by reduction or by reaction with methylmagnesium halide followed by dehydration of the resulting alcohols.

α-Methylstyrenes with ortho halogen atoms have been shown[2b] not to polymerize or copolymerize freely, a fact which is attributed to the steric hindrance to free rotation of the isopropenyl group provided by the ortho substituent. This hindrance is not as extreme in the thiophene series. The angles between adjacent positions amount to about 72° for five-membered rings and only about 60° for six-membered rings. Models show that the isopropenyl group in 2,5-dichloro-3-isopropenylthiophene is free to rotate about a full circle, and in agreement with the model and the theory this vinyl compound copolymerizes satisfactorily with butadiene in an emulsion system. That it is a borderline case is indicated by the fact that its bulk polymer with maleic anhydride and its emulsion polymer with styrene were obtained in only small yields (about 5%).

Acknowledgment.—We wish to express our appreciation to the Purdue Research Foundation and to the General Tire and Rubber Company for financial support in the form of a fellowship.

Experimental

Unsubstituted Vinylthiophenes.—2-Vinylthiophene has been previously reported.[4] 2-Isopropenylthiophene was prepared by adding 2-acetylthiophene to an ether solution of methylmagnesium bromide (a different method from that used by Thomas[5]), and steam distilling the unstable hydrolyzed product with 2% sulfuric acid.

Anal. Calcd. for C_7H_8S: C, 67.7; H, 6.5. Found: C, 67.7; H, 6.5.

5-Bromo-2-vinylthiophenes.—2,5-Dibromothiophene,[6] 182 g. (0.75 mole), in 250 ml. of dry ether was converted to the mono-Grignard reagent with 18.3 g. (0.75 mole) of magnesium. Benzene, 200 ml., caused the ether-insoluble red oil to dissolve. Addition of acetaldehyde 34 g. (0.77 mole) or acetone 43.5 g. (0.75 mole) and hydrolysis with dilute acetic acid gave the corresponding alcohols mixed

---

[1] From the Ph.D. thesis of L. V. Heisey, Purdue University, June, 1947. Present address: McPherson College, McPherson, Kansas.

[2] For previous papers in this series see, (a) Bachman and Lewis, THIS JOURNAL, **69**, 2022 (1947), and (b) Bachman and Finholt, *ibid.*, **70**, 622 (1948).

[3] Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944).

[4] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[5] Thomas, *Bull. soc. chim.*, **5**, 732 (1908); *Compt. rend.*, **146**, 642 (1908).

[6] Steinkopf and Köhler, *Ann.*, **532**, 250 (1937).