

produce downfield shifts that decrease in magnitude as the carbon under study becomes more unsaturated. When transmitted through a double bond the effect is an upfield shift.

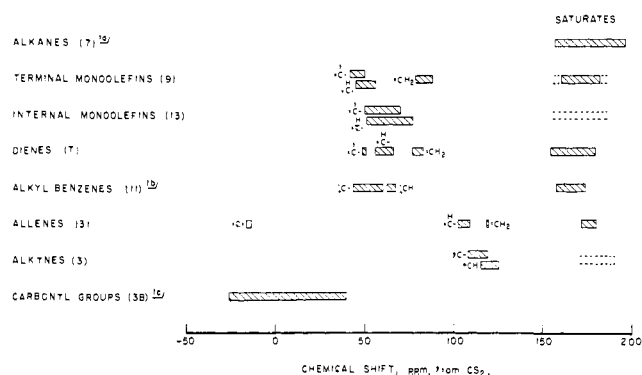


Fig. 12.—Correlation chart for  $C^{13}$  n.m.r. spectra; hydrocarbons and carbonyls: =====, range for saturate groups. Partly Bureau of Mines work; contains data from: <sup>1a</sup> ref. 7, 8, <sup>1b</sup> ref. 5, <sup>1c</sup> ref. 10.

In the case of aromatic compounds the chemical shift of the *o*- and *m*-carbons in toluene differs only slightly from the ring carbon resonance in benzene.<sup>6,8</sup> This small effect in the intermediate aromatic system appears reasonable in view of these findings. Effects transmitted through two single bonds are very small, but produce upfield shifts when one of the bonds is multiple or small downfield shifts when both are double.

**Spin-Spin Coupling.**—Fine structure in n.m.r. spectrometry can be both an advantage and a disadvantage. In the study of complex substances by  $C^{13}$  n.m.r. fine structure is sometimes a disadvantage, and it is desirable to utilize a method for collapsing the

fine structure. A method of achieving this has been described by Bloom and Shoolery<sup>14</sup>; apparatus for performing such experiments is now available. By means of 60-megacycle radiation of the hydrogens bonded to the carbon atoms, the coupling interaction between them is eliminated while the carbon-13 resonance is being recorded; in this way the fine structure is collapsed. The effect of this is shown (Fig. 11) by comparison of the spectra of  $C(CH_2CH_3)_4$  taken under ordinary  $C^{13}$  conditions and under spin-decoupling conditions with radiation of the protons at 60 megacycles. The values used in Table II for this compound were obtained by utilizing this technique. For a methyl group producing a quartet with relative intensities of 1:3:3:1 the total absorption will collapse into a single peak with a relative intensity of at least 8. Thus an appreciable gain in sensitivity is achieved. The increased sensitivity and the decrease in spectral complexity will be very useful in the study of complex materials. This technique promises to be particularly helpful in the case of coal spectra in which fine structure is more of a detriment than an advantage. Fine structure is so prolific in coal derivatives that the result is no structure at all; this is similar to the case of mass spectra of complex molecules. If some of the structure can be eliminated (in the case of mass spectrometry the answer was low-ionizing-voltage spectra) then it will be possible to produce informative spectral bands where previously no information was available. It may be possible to find absorption bands in the spectra of coal derivatives where presently, under ordinary conditions, there is only broad diffuse absorption.

**Chemical Shift Chart.**—A spectra-correlation chart (Fig. 12) summarizes the work described and illustrates the possible application to hydrocarbon structures. For comparison purposes the range of shift data for carbonyl groups is also given.

(14) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

## Hammett's Relations in Anionic Copolymerizations

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The absolute rate constants of anionic homo- and copolymerization in THF were determined for the monomers: styrene,  $\alpha$ -methylstyrene, *p*-methylstyrene, *p*-methoxystyrene, *p*-*t*-butylstyrene, *p*-fluorostyrene, *p*-chlorostyrene, 4-vinylbiphenyl, *o*-methylstyrene, 2,4-dimethylstyrene and vinylmesitylene. It was shown that the Hammett relation is obeyed by the rate constants of copolymerization of *p*-substituted styrenes with living polystyrene. The respective  $\rho = +5.0$ , while for the radical polymerization  $\rho = 0.5$  and in a coordination polymerization  $\rho = -0.95$ . The effect of polar factors and steric effects upon the rate constants of these reactions was discussed.

A technique for determining the absolute rate constants of propagation of anionic homo- and copolymerization was described in previous communications from this Laboratory.<sup>1,2</sup> Anionic polymerization, if carried out under suitable conditions, yields living polymers,<sup>3,4</sup> *i.e.*, polymeric species which resume their growth when mixed with additional monomer. The concentration of living ends may be determined by a suitable analytical or spectrophotometric technique and, in a properly conducted experiment, this concentration remains constant during the course of polymer-

ization. Since most of the anionic polymerizations proceed extremely rapidly in tetrahydrofuran, studies of such reactions require special techniques; *e.g.*, the fast flow technique, originally described by Hartridge and Roughton<sup>5</sup> could be adopted for this purpose.<sup>1</sup> The solutions of living polymers and of the investigated monomer are mixed in a suitable chamber, the mixture is then passed through a capillary, and finally the polymerization quenched at the capillary outlet by flowing the reacting solution into wet tetrahydrofuran. In this arrangement the time of polymerization may be varied from 0.05 sec. to about 2 sec. by changing the rate of flow or the volume of the capillary. The concentration of the residual monomer is then determined

(1) C. Geacintov, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 2508 (1962).

(2) D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *ibid.*, **85**, 533 (1963).

(3) M. Szwarc, M. Levy and R. Milkovich, *ibid.*, **78**, 2656 (1956).

(4) M. Szwarc, *Nature*, **178**, 1168 (1956).

(5) H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc. (London)*, **B104**, 376 (1923).

either spectrophotometrically or by V.P.C. (using a suitable internal standard), and thus all the data required for calculation of rate constants become available. All technical details pertaining to this method are described in ref. 1.

In a homopolymerization the kinetics of the monomer conversion is given by the 1st order law, since the concentration of living ends remains constant throughout the experiment. The rate constant of propagation,  $k_{11}$ , is calculated, therefore, by plotting  $[\text{Liv. ends}]^{-1} \times \ln(C_0/C_t)$  vs. time, where  $[\text{Liv. ends}]$  denotes the concentration of living ends. In a copolymerization experiment, a solution of living polymers containing the terminal  $A^-$  unit is mixed with a solution of the required monomer B. In such experiments, it is desirable to maintain the condition  $[B] < [^{\sim}A^-]$ , since then, on the average, less than one unit of B is added to  $^{\sim}A^-$  end, and therefore the initial rate of conversion gives the copolymerization rate constant  $k_{12}$ . For  $k_{12} \approx k_{22}$ , the results may be calculated from the first order kinetic equation, while for  $k_{12} \gg k_{22}$ , a second-order kinetic equation leads to a more realistic value for the respective rate constant. Both methods of calculation lead to identical results when the degree of conversion is low (less than 30%). When the kinetic data are available the most reliable method may easily be chosen for each individual case. A more elaborated discussion of these problems is found in ref. 2.

### Experimental

The following monomers were investigated: styrene, *p*-methylstyrene, *o*-methylstyrene, 2,4-dimethylstyrene, vinylmesitylene, *p*-*t*-butylstyrene, *p*-methoxystyrene, *p*-vinylbiphenyl, *p*-fluorostyrene and *p*-chlorostyrene. Samples of *p*-*t*-butylstyrene and *p*-fluorostyrene were kindly offered to us by Prof. C. G. Overberger and a sample of *p*-vinylbiphenyl was provided by Dr. A. Rembaum, both of whom we thank for their help. The first two monomers were found to be pure (tested by V.P.C.), whereas the *p*-vinylbiphenyl yielded a pure compound only after repeated recrystallizations. The remaining monomers were acquired commercially, and all were carefully fractionated at reduced pressure on a spinning band column. The middle fraction boiling at constant temperature was collected and then redistilled under high vacuum. The purity of all the fractionated monomers was tested by V.P.C. and found to be satisfactory, 2,4-dimethylstyrene being the only exception. Two small additional peaks were found close to the main peak of the latter monomer; apparently they represent some other isomeric dimethylstyrenes still present in the sample.

All the monomers were dried with calcium hydride by stirring the slurry under high vacuum for 24 hours. Thereafter, they were directly distilled on a high vacuum line into ampoules equipped with break-seals which were then sealed off the line.

The purification of the solvent is described in ref. 1 and the details will not be repeated here. Most of the investigated living polymers were produced by initiating the polymerization of the respective monomers with disodium  $\alpha$ -methylstyrene tetramer<sup>1</sup>; the living polyvinyl mesitylene was prepared by the action of Na-K alloy on the monomer solution in THF. Under our experimental conditions the average DP of the resulting polymers was about 25. The solutions were red and their absorption spectra resembled that of the unsubstituted polystyryl anions ( $\lambda_{\text{max}} \sim 340 \text{ m}\mu$ ), the largest shift in the absorption maximum was shown by living polyvinyl mesitylene ( $\lambda_{\text{max}} 360 \text{ m}\mu$ ). To avoid any "killing" of the growing ends, the solutions were used for kinetic studies within a few hours after their preparation. The living polymers produced from *p*-fluoro- and *p*-chlorostyrene were unstable; at room temperature they decomposed within a few minutes. Consequently, it was not possible to study their homopolymerization or their reactions with other monomers, and only the kinetics of their addition to living polystyrene could be investigated. However, at  $-80^\circ$  the solution of living *p*-fluorostyrene appeared to be stable for a reasonable length of time.

The experimental procedure followed in each kinetic run has been described in ref. 1. The results were calculated on the basis of the first-order kinetics<sup>6</sup> assuming a turbulent flow.<sup>1</sup> In most experiments the concentration of the residual monomer was determined spectrophotometrically. For each styrene derivative

the respective absorption peak, located in the region 290–300  $\text{m}\mu$ , was used in the analysis. The light absorption due to the polymer was compensated for by introducing the respective polymer solution into the reference cell. A linear dependence of o.d. on the concentration of the monomer was established for each monomer. Vinylmesitylene and vinylbiphenyl were analyzed by V.P.C. Also in the system  $^{\sim}p$ -methoxystyrene<sup>-</sup> + styrene it was necessary to use V.P.C. to determine the concentration of the residual styrene.

### Results

All the results obtained in this work are presented in Table I, which lists the propagation rate constants of anionic homopolymerizations, and in Table II in which the data pertaining to the anionic copolymerizations are collected, all the results being obtained in THF solution. Inspection of Table I shows that the bimolecular rate constants,  $k_{ij}$ , defined by the equation

$$-d[M]/dt = k_{ij}[M][\text{Liv. ends}]$$

TABLE I  
KINETICS OF ANIONIC HOMOPROPAGATION  
Solvent, THF;  $T$ ,  $25^\circ$ ; counter-ion,  $\text{Na}^+$

Monomer	[Living ends], $\times 10^3$ m./l.	[M], $\times 10^2$ m./l.	Conver., %	No. of points	$k$ , l. m. <sup>-1</sup> sec. <sup>-1</sup>
<i>p</i> -Methylstyrene	1.8	23	37–55	4	264
<i>p</i> -Methylstyrene	2.9	22	47–71	4	223
<i>p</i> -Methylstyrene	3.5	23	44–63	4	178
<i>p</i> -Methylstyrene	6.0	23	63–81	4	166
<i>o</i> -Methylstyrene	2.6	21	26–50	5	168
<i>o</i> -Methylstyrene	5.3	26	40–69	5	127
<i>p</i> - <i>t</i> -Butylstyrene	2.8	4.1	58–88	5	223
<i>p</i> -Methoxystyrene	3.3	16.3	13–28	4	51.5
<i>p</i> -Methoxystyrene	5.9	16.3	19–36	5	40.0
<i>p</i> -Methoxystyrene	8.8	16.3	26–40	4	37.6
Vinylmesitylene <sup>a</sup>	5.9	28.0	23–67	5	0.34

<sup>a</sup>  $\text{K}^+$  as the counter-ion.

are affected by the initial concentrations of the reagents, e.g.,  $k_{ij}$  slightly increases with decreasing concentration of living ends. This dependence of the apparent rate constant of propagation upon  $[\text{Liv. ends}]$  was reported in a previous paper describing the anionic polymerization of styrene.<sup>1</sup> A similar trend was observed in the anionic copolymerizations; see Table II. In a forthcoming paper it will be shown that  $k_{ij}$  (or  $k_{ij}$ ) is a slowly varying function of the product  $[M][\text{Liv. ends}]$ ; e.g.,  $k$  increases by about a factor of 2 when this product decreases by about a factor of 100. The cause of this behavior will be discussed in that paper; however, at this time we wish to stress that the rate constants  $k_{ij}$  have to be compared for corresponding states of the systems, since  $k_{ij}$ 's are not rigorously constant. The correlations shown in Tables III, IV and V refer, e.g., to the rate constants obtained for  $[\text{Liv. ends}] \approx 3 \times 10^{-3}$  m./l. and, if possible, for similar or slightly smaller values of  $[M]$ . The choice of these conditions is rather arbitrary and perhaps not the most satisfactory; fortunately, the variation of each  $k_{ij}$  is not too great, and hence the pattern emerging from our data cannot be affected by this particular choice.

Most of the reported experiments were performed in the capillary flow system. The addition of *p*-methoxystyrene to living polystyrene was investigated in a stirred flow reactor as well as by the capillary flow technique. The details of the stirred reactor technique will be reported elsewhere. It should be noticed, however, that similar results were obtained by both techniques. The slow homopolymerization of vinylmesitylene as well as its slow addition to living polystyrene forced us to use a batch technique for those experiments.

(6) Slightly higher rate constants are obtained when the second-order kinetic law is assumed. It appears, however, that for these systems the first-order law gives a more correct value for the copolymerization rate constants.

TABLE II  
KINETICS OF ANIONIC CROSS-PROPAGATION  
Solvent, THF;  $T$ , 25°; counter-ion, Na<sup>+</sup>

Growing end	$[M_1^-]$ , $\times 10^3$ m./l.	Monomer	$[M_2]$ , $\times 10^3$ m./l.	Conv., %	No. of points	$k_{12}$ , l. m. <sup>-1</sup> sec. <sup>-1</sup> <sup>a</sup>
Styrene <sup>-</sup>	2.4	<i>p</i> -Methylstyrene	2.2	27-46	4	189
Styrene <sup>-</sup>	2.7	<i>p</i> -Methylstyrene	3.3	38-55	4	181
Styrene <sup>-</sup>	5.1	<i>p</i> -Methylstyrene	7.8	23-59	3	157
Styrene <sup>-</sup>	8.4	<i>p</i> -Methylstyrene	5.3	60-78	4	129
Styrene <sup>-</sup>	2.7	<i>p</i> -Methoxystyrene	2.5	33-66	4	49 <sup>b</sup>
Styrene <sup>-</sup>	3.4	<i>p</i> -Methoxystyrene	2.5	40-74	6	55 <sup>b</sup>
Styrene <sup>-</sup>	5.0	<i>p</i> -Methoxystyrene	2.5	12-22.5	5	34
Styrene <sup>-</sup>	8.6	<i>p</i> -Methoxystyrene	3.9	15-29	5	25
Styrene <sup>-</sup>	2.85	<i>p-t</i> -Butylstyrene	2.95	33-57	5	110
Styrene <sup>-</sup>	4.8	<i>p-t</i> -Butylstyrene	2.95	56-76	5	110
Styrene <sup>-</sup>	0.85	<i>p</i> -Fluorostyrene	0.75	5.2-10	5	2300
Styrene <sup>-</sup>	1.7	<i>p</i> -Fluorostyrene	1.35	18-35	5	1960
Styrene <sup>-</sup>	2.8	<i>p</i> -Fluorostyrene	2.0	23-47	5	1800
Styrene <sup>-</sup>	0.76	<i>p</i> -Chlorostyrene	1.1	48-70	6	23000
Styrene <sup>-</sup>	2.6	<i>o</i> -Methylstyrene	2.4	24-33	4	540
Styrene <sup>-</sup>	4.5	<i>o</i> -Methylstyrene	3.0	33-50	5	520
Styrene <sup>-</sup>	3.1	Vinylmesitylene	1.3	18-43	5	0.92 <sup>c</sup>
Styrene <sup>-</sup>	3.0	2,4-Dimethylstyrene	2.2	39-58	5	161
Styrene <sup>-</sup>	3.3	2,4-Dimethylstyrene	3.8	39-61	5	156
Styrene <sup>-</sup>	4.8	2,4-Dimethylstyrene	3.8	48-73	5	138
Styrene <sup>-</sup>	7.6	2,4-Dimethylstyrene	6.0	59-80	5	108
Styrene <sup>-</sup>	2.6	<i>p</i> -Vinylbiphenyl	3.4	24-44	5	1700
Styrene <sup>-</sup>	2.95	<i>p</i> -Vinylbiphenyl	1.9	24-43	5	1660
Styrene <sup>-</sup>	5.5	<i>p</i> -Vinylbiphenyl	3.6	53-71	5	2000
Vinylmesitylene <sup>-d</sup>	3.4	Styrene	2.55	20-44	7	77
<i>p</i> -Methylstyrene <sup>-</sup>	2.8	Styrene	2.2	21-36	5	1230
<i>p</i> -Methylstyrene <sup>-</sup>	4.8	Styrene	4.2	31-52	5	965
<i>p</i> -Methylstyrene <sup>-</sup>	5.5	Styrene	5.1	30-50	5	925
<i>p</i> -Methylstyrene <sup>-</sup>	7.0	Styrene	4.7	37-52	3	865
<i>p</i> -Methylstyrene <sup>-</sup>	8.7	Styrene	4.2	46-69	5	835
<i>p</i> -Methoxystyrene <sup>-</sup>	3.1	Styrene	1.8	29-40	3	1140
<i>p</i> -Methoxystyrene <sup>-</sup>	3.4	Styrene	1.9	26-37	5	1060
<i>p</i> -Methoxystyrene <sup>-</sup>	5.4	Styrene	2.7	31-50	4	940
<i>p</i> -Methoxystyrene <sup>-</sup>	7.5	Styrene	5.1	31-54	5	745

<sup>a</sup> Calculated on the basis of first-order kinetics. <sup>b</sup> These runs were carried out in a stirred flow reactor. <sup>c</sup> This run was carried out in a batch system. <sup>d</sup> K<sup>+</sup> as the counter-ion.

TABLE III

FOUR COPOLYMERIZATION RATE CONSTANTS AND REACTIVITIES RATIO

Solvent, THF; $T$ , 25°; counter-ion, Na <sup>+</sup>					
[Living ends] = $3 \times 10^{-3}$ m./l.; [monomer] = $2-3 \times 10^{-3}$ m./l.					
Rate constants given in units l. m. <sup>-1</sup> sec. <sup>-1</sup>					
M <sub>1</sub>	$k_{11}$	$k_{12}$	M <sub>2</sub>	$k_{21}$	$k_{22}$
Styrene	950	180	<i>p</i> -Methylstyrene	1150	210 <sup>a</sup>
$r_1 = 5.3, r_2 = 0.18, r_1 \times r_2 \sim 1$					
Styrene	950	50	<i>p</i> -Methoxystyrene	1100	50 <sup>b</sup>
$r_1 = 19, r_2 = 0.045, r_1 \times r_2 = 0.85$					
Styrene	950	0.9	Vinylmesitylene	77	0.3 <sup>c</sup>
$r_1 = 1060, r_2 = 4 \times 10^{-3}, r_1 \times r_2 \sim 4$					

<sup>a</sup>  $[M_2] = 22 \times 10^{-3}$  m./l. <sup>b</sup>  $[M_2] = 16 \times 10^{-3}$  m./l. <sup>c</sup>  $[M_2] = 28 \times 10^{-3}$  m./l.

### Discussion

All the four copolymerization rate constants were determined for three pairs of monomers; namely, styrene-*p*-methylstyrene, styrene-*p*-methoxystyrene and styrene-vinylmesitylene (see Table III). The first two systems were recently investigated by Tobolsky and Boudreau,<sup>7</sup> who calculated the respective reactivity ratios  $r_1$  and  $r_2$  from the composition of the copolymers. The following results were reported for the reaction

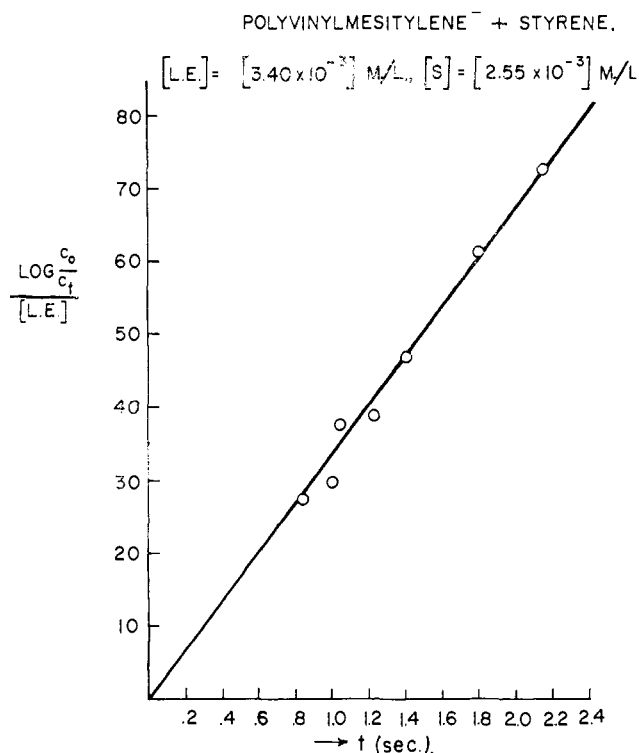
(7) A. V. Tobolsky and R. J. Boudreau, *J. Polymer Sci.*, **51**, S 53 (1961).

TABLE IV

ADDITION OF SUBSTITUTED STYRENE TO LIVING POLYSTYRENE  
Solvent, THF;  $T$ , 25°; counter-ion, Na<sup>+</sup>; [liv. ends]  $\sim 3 \times 10^{-3}$  m./l.;  $[M] \leq$  [liv. ends]

Monomer	$k_{ij}$	$\sigma$	Ref. and remarks
Vinylmesitylene	1	.....	This work
$\beta$ -Methylstyrene	18	.....	<sup>a</sup> ; [L.e.] = 5.3
$\alpha$ -Methylstyrene	27	.....	<sup>a</sup>
<i>p</i> -Methoxystyrene	50	-0.268	This work
<i>p-t</i> -Butylstyrene	110	-0.197	This work
2,4-Dimethylstyrene	160	.....	This work
<i>p</i> -Methylstyrene	180	-0.170	This work
<i>o</i> -Methylstyrene	530	.....	This work
Styrene	950	0.000	<sup>b</sup> ; $[M] \approx$ [Liv. ends]
1,1-Diphenylethylene	2400	.....	<sup>c</sup>
4-Vinylbiphenyl	1700	+0.03 <sup>f</sup>	This work
<i>p</i> -Fluorostyrene	1800	+0.062	This work
1-Vinylnaphthalene	8000	+0.170	<sup>d</sup>
<i>p</i> -Chlorostyrene	23000	+0.227	This work; [L.e.] = 0.8
2-Vinylpyridine	>>50000	.....	<sup>e</sup> ; } probable values
4-Vinylpyridine	>>50000	.....	<sup>e</sup> ; } of $k_{ij} \sim 10^5$

<sup>a</sup> D. N. Bhattacharyya, C. L. Lee, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 533 (1963). <sup>b</sup> C. Geacintov, J. Smid and M. Szwarc, *ibid.*, **84**, 2508 (1962). <sup>c</sup> E. Ureta, unpublished work from this Laboratory. <sup>d</sup> F. Bahsteter, unpublished work from this Laboratory. <sup>e</sup> C. L. Lee, J. Smid and M. Szwarc, *Trans. Faraday Soc.*, in press. <sup>f</sup> The  $\sigma$ -value is calculated from the  $k_{ij}$  found in this study; the data reported in the literature range from  $\sigma = -0.1$  to  $\sigma = +0.1$ .



proceeding in THF at 0° with Na<sup>+</sup> as the counter-ion for the system styrene-*p*-methylstyrene:  $r_1 = 1.97$  and  $r_2 = 0.38$  for the system styrene-*p*-methoxystyrene:  $r_1 = 4.1$  and  $r_2 = 0.13$

Our rate constants led to  $r_1 = 5.3$  and  $r_2 = 0.18$  for styrene-*p*-methylstyrene and to  $r_1 = 19$  and  $r_2 = 0.18$  for styrene-*p*-methoxystyrene. The agreement between both sets of data is fair if one recalls that our experimental conditions were different from those maintained in Tobolsky's studies, and that the conventional method of determining the reactivity ratios  $r_1$  and  $r_2$  might be uncertain when applied to anionic copolymerization.<sup>8</sup> It is gratifying to notice that in

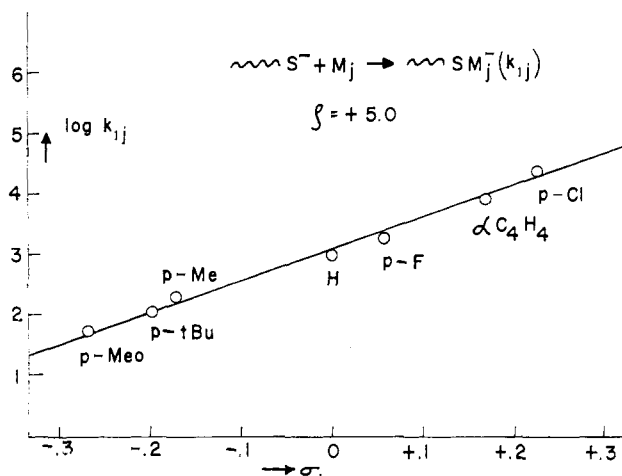
TABLE V

ADDITION OF STYRENE (1) TO VARIOUS ANIONS ( <i>j</i> )		
Solvent, THF; <i>T</i> , 25°; counter-ion, Na <sup>+</sup>		
Anion	$k_{j1}$ , l./mole sec.	Ref. and remarks
<i>p</i> -Methoxystyrene <sup>-</sup>	1100	This work
<i>p</i> -Methylstyrene <sup>-</sup>	1150	This work
Styrene <sup>-</sup>	950	Ref. 1
$\alpha$ -Methylstyrene <sup>-</sup>	~500	This work, tetramer
Vinylmesitylene <sup>-</sup>	77	This work, K <sup>+</sup> counter-ion
1,1-Diphenylethylene <sup>-</sup>	0.3-1	Ureta, unpublished work from this Laboratory
2-Vinylpyridine <sup>-</sup>	Very low	Lee, Smid and Szwarc; <i>Trans. Faraday Soc.</i> , in press

both investigations the spread between  $r_1$  and  $r_2$  increased when *p*-methoxystyrene was substituted for *p*-methylstyrene. This trend was indeed anticipated. The products  $r_1 \cdot r_2$  calculated from our data are close to unity. This also is reasonable since these monomers are very alike.

The system styrene-vinylmesitylene is more complex. The two *o*-methyl groups prevent the coplanarity of the vinylmesitylene molecule, and this is reflected in its low

(8) R. K. Graham, D. L. Dunkelberger and W. E. Goode, *J. Am. Chem. Soc.*, **82**, 400 (1960).



reactivity toward methyl radical addition.<sup>9</sup> However, inspection of models shows that the resonance stabilization of the respective carbanion may be substantial if its configuration is tetrahedral. The similarity of the absorption spectrum of this anion ( $\lambda_{\max}$  360 m $\mu$ ) with that of the polystyryl anion ( $\lambda_{\max}$  340 m $\mu$ ) may be considered as evidence for a high degree of resonance stabilization of the carbanion albeit not of the transition state of the addition process. Hence, vinylmesitylene is expected to be an unreactive monomer which forms a relatively unreactive anion. The observed rate constants reflect qualitatively this relation, although the values of  $k_{21}$  and  $k_{22}$  (see Table III) are still lower than anticipated. The reason for this behavior is obscure; most probably it results from some steric hindrances associated with the two *o*-methyl groups. However, further studies of this subject might be desirable. One should notice also that in this system  $k_{21} \ll k_{11}$ . Nevertheless, the plot of  $[LE]^{-1} \log [S_0/S]$  vs. time gives a good straight line (see Fig. 1) up to 35% conversion of  $\sim$ vinylmesit<sup>-</sup> into  $\sim$ S<sup>-</sup>. This may not be significant because up to 30% conversion the first-order and second-order plots coincide within experimental error.

The rate constants of addition of various substituted styrenes to living polystyrene in THF are listed in Table IV. One anticipates that the respective  $k_{ij}$  should obey the Hammett relation, and indeed this is shown in Fig. 2. The experimental points fit well a straight line corresponding to  $\rho = +5.0$ .

There is a substantial scatter in the  $\sigma$ -values reported in the literature for the *p*-phenyl substituent; they seem to range from -0.1 to +0.1. Our results for 4-vinylbiphenyl lead to a reasonable value of  $\sigma = +0.03$ .

The high positive  $\rho$ -value characterizing the anionic copolymerization should be compared with  $\rho = +0.5$  found for the same series of substrates in a radical copolymerization.<sup>10</sup> These values show that both species behave as nucleophilic reagents, although, as expected, the selectivity of a carbanion is much greater than that of a radical. On the other hand, copolymerization studies with the same series of substrates initiated by coordination catalysts<sup>11</sup> led to the negative value of  $\rho = -0.95$ . Hence, in this intrinsically anionic polymerization the coordination between monomer and the electron-deficient part of the reactive center seems to be the rate-determining step,<sup>11</sup> while

(9) F. Carrock and M. Szwarc, *ibid.*, **81**, 4138 (1959).

(10) C. Walling, F. R. Mayo, *et al.*, *ibid.*, **70**, 1537 (1948).

(11) G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, **30**, 238 (1959).

TABLE VI

THE RATE CONSTANTS OF COPOLYMERIZATION OF STYRENE DERIVATIVES WITH DIANION OF  $\alpha$ -METHYLSTYRENE TETRAMER  $\text{Na}^+$ ,  $-\text{C}(\text{CH}_3)(\text{Ph})\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})\text{C}(\text{CH}_3)(\text{Ph})\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})^-$ ,  $\text{Na}^+$  + M  $\rightarrow$   $\text{Na}^+$ ,  $-\text{C}(\text{CH}_3)(\text{Ph})\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})\text{C}(\text{CH}_3)(\text{Ph})\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})\text{M}^-$ ,  $\text{Na}^+$   
Solvent, THF; T, 25°

Monomer	[Liv. ends], $\times 10^3$ m./l.	[M], $\times 10^3$ m./l.	Conv., %	$k_{ij}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
Styrene	3.0	1.4	...	500 <sup>a</sup>
Styrene	3.7	2.4	...	520 <sup>a</sup>
<i>p</i> -Methylstyrene	3.3	2.1	6-15	105
<i>p</i> -Methylstyrene	5.9	4.9	12-20	82
<i>p</i> -Methoxystyrene	2.6	2.4	23-57	28 <sup>b</sup>

<sup>a</sup> These data, calculated from the V.P.C. analysis of the residual styrene, are lower than those obtained previously (800-1000). We feel that the spectrophotometric technique used in the earlier investigations could be less reliable, since the tetramer solution acquired a slightly yellow color on standing in air. <sup>b</sup> This system was studied in a stirred-flow reactor.

in the ordinary anionic polymerization this step apparently involves a negative center.

The low reactivities of  $\alpha$ - and  $\beta$ -methylstyrenes reflect the effect of steric hindrance due to the presence of a methyl group located close to the center of reaction. This effect is superimposed upon the inductive effect which also reduces the rate of copolymerization.

The higher reactivity of *o*-methylstyrene when compared with its *p*-isomer is unexpected and the cause of

this trend is not clear. The lower reactivity of 2,4-dimethylstyrene could be anticipated in view of the enhanced inductive effect of two methyl substituents.

The pattern observed in the rate constants of copolymerization of styrene derivatives with living polystyrene is reflected in the respective rate constants of addition to the living  $\alpha$ -methylstyrene tetramer ( $\text{Na}^+$ ,  $-\text{C}(\text{CH}_3)(\text{Ph})\text{CH}_2\text{CH}_2[\text{C}(\text{CH}_3)(\text{Ph})]_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{Ph})^-$ ,  $\text{Na}^+$ ). The pertinent results are collected in Table VI, and it is interesting to notice that all the values given in this table are lower by approximately a factor of 2 than the corresponding values related to the addition to living polystyrene. On the other hand, the addition of styrene to poly-*p*-methylstyrene<sup>-</sup> or poly-*p*-methoxystyrene<sup>-</sup> (see Table V) proceeds as fast as the addition to the living polystyrene. It seems, therefore, that the steric factor is mainly responsible for the lower rate constants of addition to the tetramer of  $\alpha$ -methylstyrene.

Finally, it should be pointed out that the results collected in Table V indicate that the polar factors are less important when they operate on the anion than when they act on the monomer (compare the rate constants of copolymerization of the pairs: styrene-*p*-methylstyrene and styrene-*p*-methoxystyrene). They become, however, significant when the polarity of the anion is changed considerably, e.g., in the addition of styrene to the living polyvinylpyridine.

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## F<sup>19</sup> Chemical Shifts of the Sulfur Pentafluoride, Trifluoromethoxy, Trifluoromethylthio and Trifluoromethylsulfonyl Groups in Aromatic Compounds

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The F<sup>19</sup> n.m.r. spectra have been measured for a series of arylsulfur pentafluorides and aryl trifluoromethyl ethers, sulfides and sulfones substituted in the *meta* or *para* position. The twenty-one line pattern for the sulfur pentafluoride group was analyzed as an AB<sub>4</sub> system, and the chemical shift and spin-spin coupling constants determined. The coupling constant of 146 c.p.s. between the base and apex fluorine is independent of the substituent. The F<sup>19</sup> chemical shifts of these groups have been correlated with Hammett  $\sigma$ -factors and with Taft's inductive and resonance parameters. The magnitudes of the changes in chemical shift with substituent and the correlations with reactivity parameters are discussed.

### Introduction

A number of correlations between chemical reactivity and physical properties, such as vibrational band frequencies and intensities, polarographic half-wave potentials and n.m.r. chemical shifts, have been observed and explored in recent years. Of these physical properties, the study of the F<sup>19</sup> n.m.r. chemical shifts is particularly attractive because of the high precision of the measurements and the relatively direct relationship to chemical bonding. Gutowsky, McCall, McGarvey and Meyer<sup>1</sup> first noted the correlation of the fluorine chemical shifts with Hammett  $\sigma$ -constants for a series of substituted fluorobenzenes. Taft<sup>1b,2,3</sup> has extended and elaborated this correlation by interpreting the shifts in terms of inductive and resonance effects. Theoretical treatments of the problem have been presented recently by several groups.<sup>4</sup>

(1) (a) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); (b) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 323.

(2) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(3) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

There is, however, very little experimental data available on the chemical shifts of fluoroaromatics other than the fluorobenzenes.<sup>5</sup> It is the purpose of the present study to investigate the possible correlation of the F<sup>19</sup> chemical shifts of the SF<sub>5</sub>, OCF<sub>3</sub>, SCF<sub>3</sub> and SO<sub>2</sub>CF<sub>3</sub> groups and the spin-spin coupling constant of the SF<sub>5</sub> group with substituent parameters. Such data should provide a further test of the validity of current theories of aromatic substitution effects and also should give some information on the transmission of inductive and mesomeric interactions through oxygen and sulfur atoms.<sup>6</sup> A concurrent study has been made of the

(4) (a) M. Karpius and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961); (b) T. Yonezawa, K. Fukui, H. Kato, H. Kilano, S. Hattori and S. Matsuoka, *Bull. Chem. Soc. Japan*, **34**, 707 (1961); (c) R. W. Taft, F. Prosser, L. Goodman and G. T. Davis, *J. Chem. Phys.*, **38**, 380 (1963).

(5) A limited amount of chemical shift data has been reported on benzo-trifluorides<sup>1a</sup> and on aryl trifluoromethyl ethers, sulfides and sulfones; L. M. Yagupolsky, V. F. Bystrov and E. Z. Utyanskaya, *Proc. Acad. Sci. USSR, Phys. and Chem. Sect. (Engl. Transl.)*, **135**, 1059 (1960), and *Optics and Spectroscopy*, **10**, 68 (1961). Correlations of proton chemical shift with Hammett  $\sigma$ -parameters for the methyl group of *m*- and *p*-substituted anisoles were recently reported by C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

(6) The substituent parameters for the groups along with the synthetic