acid. The chloride was purified by repeatedly precipitating it from chloroform solutions by adding hexane and later by adding ether. At the end of this treatment the chloride was a fine crystalline powder with a metallic luster.

The chloride was dissolved in methanol and converted to the methyl ether by adding sodium methylate. After it had stood sufficiently long to allow all of the anhydro base to change to the methyl ether, the methyl ether was precipitated with water. The methyl ether was dissolved in chloroform. The solution was boiled with nuchar 00 and filtered. The chloroform was evaporated off. The resulting methyl ether was further decolorized by dissolving in methanol and boiling the solution with nuchar 00. This was repeated until the solution was quite colorless. Finally the methyl ether was precipitated from the solution with water, and dried *in vacuo*. The product was a white powder, m. p. 102–104°.

Anal. Calcd. for $C_{28}H_{26}N_2O$: C, 82.7; H, 6.45; N, 6.89. Found: C, 82.5, 82.4; H, 6.30, 6.27; N, 6.95, 7.02.

3,3′-Dicarbazylphenylmethyl Methyl Ether.—Two moles of carbazole, two moles of aluminum chloride, a mole of hydrochloric acid in saturated ethereal solution and 800 ml. of isoöctane were mixed in a vessel fitted with a stirrer, a dropping funnel and a reflux condenser equipped with a drying tube. The flask was placed on a steam-bath and one mole of benzotrichloride added through the dropping funnel. The stirring and the heating were continued for eight hours. The isoöctane was decanted and the reaction product dissolved in methanol. After filtration, the solution was added to a large excess of aqueous 2 *N* hydrochloric acid solution. The precipitated chloride of the dye was purified by repeated precipitation from chloroform solutions with ether. The purified chloride was a fine crystalline powder with a red metallic luster.

The chloride was dissolved in methanol and converted to the methyl ether with sodium methylate, allowing it to stand until all the anhydro base had disappeared. The methyl ether was precipitated from the solution with water. The precipitated methyl ether was dissolved in benzene and the solution filtered. The benzene was removed by evaporation *in vacuo*. The methyl ether was decolorized by boiling a methanol solution of it with nuchar 00. Finally the methyl ether was precipitated from the solution with water, filtered and dried *in vacuo*. The product was a white powder; m. p. 160–165°.

Anal. Calcd. for $C_{32}H_{24}N_2O$: C, 84.9; H, 5.35. Found: C, 84.7, 84.7; H, 5.30, 5.34.

Summary

The two dyes, N-dimethyl-*p*-aminophenyl-3-carbazylphenylmethyl chloride and 3,3′-dicarbazylphenylmethyl chloride, have been prepared and their absorption spectra measured. The spectrum of the former dye was found to vary considerably with the solvent; thus λ_x was 629 mμ in chloroform and 562 mμ in water.

The spectrum of the symmetrical dye was found to be nearly independent of the solvent. The value of λ_x was found to be less and that of λ_y greater than for the corresponding bands of malachite green.

The ultraviolet spectrum of the monocarbazyl dye in water showed the existence of a benzenoidal ion in equilibrium with the quinoidal ion.

The spectra of the anhydro bases of both dyes were also measured. In water solution the anhydro base of the monocarbazyl dye absorbs at a longer wave length than the dye itself.

The relationships between these spectra and those of malachite green and phenylated diaminotriphenylmethane dyes have been discussed.

BERKELEY, CALIFORNIA RECEIVED JUNE 19, 1945

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. II. The Copolymerization of Acrylonitrile, Methyl Methacrylate, Styrene and Vinylidene Chloride

BY FREDERICK M. LEWIS, FRANK R. MAYO AND WILLIAM F. HULSE[1]

A previous paper from this Laboratory[2] showed that the composition of the copolymer being formed, d [S]/d [M], from two monomers at concentrations [S] and [M] should be represented by the copolymerization equation

$$\frac{d[S]}{d[M]} = \frac{[S]}{[M]} \cdot \frac{\sigma[S] + [M]}{\mu[M] + [S]}$$

where σ and μ are the *monomer reactivity ratios* for radicals ending in S and M units, respectively.[3] Each monomer reactivity ratio was defined as the ratio of the rate constants for the reaction of the chosen radical type with the corresponding monomer and with the other monomer of the pair, respectively. The use of an integrated form of this equation was described and the equation was shown to account for the copolymerization of styrene and methyl methacrylate by a free radical mechanism over a wide range of monomer mixtures, conversions, and rates of polymerization. The present paper describes a study of other binary systems of the monomers acrylonitrile, methyl methacrylate, styrene and vinylidene chloride and shows how monomer reactivity ratios of radicals may be used to compare reactivities of various ethylene bonds with free radicals.

Experimental

Monomers.—The styrene and methyl methacrylate samples were like those used for most of the experiments in the previous paper.[2] Acrylonitrile was a commercial product which had been carefully fractionated; b. p. 77.0° (760 mm.), n^{20}_D 1.3931. Vinylidene chloride was

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[1] Ensign, U. S. N. R.

[2] F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

[3] Similar equations have been derived independently by T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944), and by F. T. Wall, THIS JOURNAL, **66**, 2050 (1944). The *A* and *B* of Alfrey and Goldfinger in their second paper correspond to our *S* and *M*, their $1/\alpha$ and $1/\beta$ to our σ and μ. The *X*, *Y*, σ, and ρ of Wall correspond to our *S*, *M*, σ, and μ. R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944), have presented more complicated and detailed treatments of copolymerization.

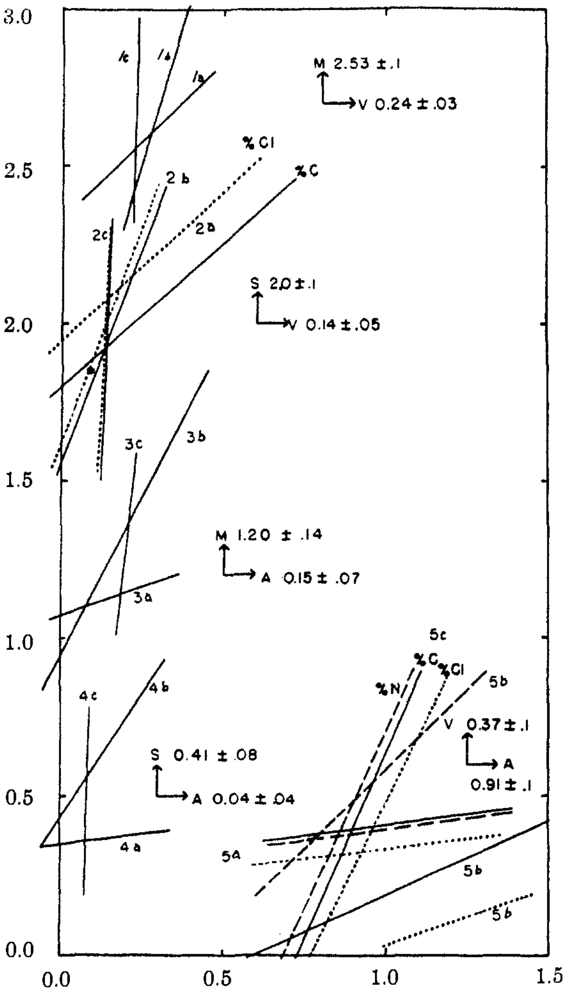

Fig. 1.—Monomer reactivity ratios of radicals in benzoyl peroxide-catalyzed copolymerizations at 60°. For each monomer pair the radical types corresponding to ordinate and abscissa are indicated by A, M, S and V for acrylonitrile, methyl methacrylate, styrene and vinylidene chloride.

prepared by the action of potassium hydroxide on 1,1,2-trichloroethane in absolute alcohol. The product was washed and fractionally distilled in a conventional manner; b. p. 30.5–30.8° (770 mm.), $n^{20}{}_{D}$ 1.4232.

Procedure.—The experimental procedures did not differ significantly from those described previously.[2] All reaction mixtures contained 0.1 mole per cent. of benzoyl peroxide and about 0.1 mole of monomers. Polymerizations were carried out at 60° in the absence of air, and all of the polymers not containing acrylonitrile were isolated by repeated precipitation from benzene solution with methanol and use of the frozen benzene technique (which has since been described in more detail[4]).

All the polymers containing acrylonitrile precipitated from solution as they formed unless the polymerizations were stopped in the very early stages. These polymers were generally isolated by dissolving in N,N-dimethylformamide, precipitating with methanol or petroleum ether, repeating the solution and precipitation twice, and then heating for four to five days at 60–70° and 1–2 mm. pressure until they reached constant weight.

All polymers were analyzed to determine their monomer contents, and the final amounts of unreacted monomers in the reaction mixtures (Table I) were calculated from the initial amounts and the amounts appearing in the polymers. In experiments 2 and 5, separate calculations are based on each of two or three different analyses. Difficulties in analyses were encountered only with the acrylonitrile–vinylidene chloride copolymers.

Analyses of Acrylonitrile–Vinylidene Chloride Copolymers.—The first acrylonitrile–vinylidene chloride copolymers were analyzed for chlorine (by heating with a calcium oxide–calcium nitrate mixture) and nitrogen (by Kjeldahl method) but the monomer proportions calculated from the two sets of results disagreed. It was thought that the copolymer might have lost hydrogen chloride. In experiment 5 in Table I, it was established that no significant amount of free hydrogen chloride appeared during either the polymerization or the isolation of the polymer by the frozen benzene technique. The recorded chlorine analyses were obtained by burning the sample in air and absorbing the combustion products. The lime fusion method gave markedly lower, and sometimes unreproducible, results on the same samples. The recorded nitrogen analyses were obtained by the Kjeldahl method. Nitrogen analyses by the Dumas method were only 60–85% as large as those recorded, even though they seemed to be reproducible. The unsatisfactory analyses of these polymers are probably due to the use of solid oxidizing agents and to the difficulty in obtaining finely divided samples.

Even the Kjeldahl analyses in sample 5b show very poor agreement, but all the polymer was used up in analyses. The average of these four analyses, 11.32%, was used for the calculations, but it is possible that the highest analysis may be a better value. To make lines 5b-N and 5b-Cl coincide with line 5b-C in Fig. 1 (and to make the analyses total 100%), the sample should contain 13.4% N and 36.0% Cl.

Results and Discussion

The experimental data are recorded in Table I. The monomer reactivity ratios of the radicals are determined graphically in Fig. 1, using the data in the table and the integrated form of the copolymerization equation. Since the choice of which monomer of each pair shall be taken as S in the copolymerization equation is perfectly arbitrary, we are not identifying σ or μ with any particular radicals. In Figure 1, the monomer reactivity ratio of the indicated radical of each pair (monomer named first of that pair in Table I) is plotted as ordinate; the monomer reactivity ratio of the second radical is plotted as abscissa.

Each line (extending indefinitely in both directions) in Fig. 1 represents the values of the monomer reactivity ratios of the radicals which satisfy the experimental data for the corresponding run in Table I. In general, the starting mixtures contained 80, 50 and 20 mole per cent. of the monomer to which the ordinate corresponds and the slopes of the corresponding lines increase as the proportion of that monomer decreases. The intersection of any two lines in one experiment represents the unique values of the monomer reactivity ratios which satisfy both runs. If the copolymerization equation and the experimental work were perfect, then lines for the three runs in one experiment would all intersect at a point. Fig. 1 shows that the three runs give instead three pairs of values in each experiment, the three points defining a triangle.

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[4] F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

TABLE I

COPOLYMERIZATIONS WITH 0.1 MOLE PER CENT. BENZOYL PEROXIDE AT 60°

Expt.	Moles of unreacted monomers Initial	Final	Initial	Final	Time, hr.	Yield, wt. %	Polymer analyses, %		
	Methyl methacrylate		Vinylidene chloride						
1a	0.0639	0.01953	0.0160	0.01034	5.0	62.8	Cl,	8.0	8.1
b	.03998	.0209	.0400	.03198	6.5	34.2	Cl,	21.2	21.4
c	.01599	.003485	.0640	.0427	11.0	42.7	Cl,	45.5	45.8
	Styrene		Vinylidene chloride						
2a	0.06325	0.03425	0.02135	0.01617	22.0	40.70	C,[a]	82.66	82.62
		.03404		.01640			Cl,	10.03	9.87
b	.04547	.02773	.04070	.03370	25.5	29.10	C,[b]	74.14	74.12
		.02767		.03379			Cl,	19.46	19.35
c	.01595	.00937	.06721	.05918	25.5	17.93	C,[c]	56.06	56.38
		.00932		.05925			Cl,	38.73	38.79
	Methyl methacrylate		Acrylonitrile						
3a	0.0652	0.0536	0.0170	0.0147	3.5	17.23	N,	2.60	2.49
b	.0405	.0325	.0387	.0346	3.5	16.68	N,	5.69	5.80
c	.0164	.0129	.0638	.0590	3.5	11.97	N,	11.00	11.17
	Styrene		Acrylonitrile						
4a	0.06390	0.05155	0.01597	0.01102	8.0	20.61	N,	4.48	4.48
b	.03995	.03060	.03995	.03340	4.7	21.25	N,	7.11	7.06
c	.01595	.00263	.06390	.04430	4.7	48.00	N,	11.40	11.23
	Vinylidene chloride		Acrylonitrile						
5a	0.1018	0.0876	0.02701	0.02028	11.0	15.62	C[g,d]	35.67	35.40
		.0876		.02032			N,	6.57	6.50
		.0880		.01971			Cl,[g]	53.19	53.55
b	.0863	.0678	.0773	.0500	5.5	26.80	C[g,e]	46.60	46.83
		.0648		.0543			N,	11.42	12.24
								11.00	10.63
		.0694		.0478			Cl,[g]	32.80	33.09
c	.0443	.0266	.1079	.0605	5.5	42.40	C[g,f]	52.83	53.07
		.0265		.0606			N,	17.18	17.16
		.0271		.0597			Cl,[g]	24.46	24.85

[a,b,c] Found: 7.00,[a] 7.11,[a] 6.27,[b] 6.29,[b] 4.70,[c] 4.80[c]% H; total of average analyses for C, H, Cl, 99. 69%,[a] 99.82%,[b] 99.73%.[c] [d,e,f]Found: 3.75,[d] 3.81,[d] 4.91,[e] 4.80,[e] 4.66,[f] 4.86[f]% H[g]; total of average analyses for C, H, N, Cl, 99.23%,[d] 95.85%,[e] 99.54%[f]. [g] Micro analyses by Dr. T. S. Ma, Department of Chemistry, University of Chicago.

It was shown previously[2] that the position of the lines in the plots is very sensitive to errors in analyses. Calculation of run 3b on the basis that the polymer contains 6.00% N instead of 5.75% N gives a line of the same slope as 3B but passing through $\mu = 0.2$, $\sigma = 1.15$, barely to the right of the intersection of lines 3a and 3c. Similar considerations in experiments 1, 2, and 4 show that these sets of lines also intersect at points within experimental error. In experiment 2, the polymers were analyzed by two independent methods and the results are in good agreement. In experiment 5, analytical difficulties were encountered, as described in the Experimental Part. Here, the values of the monomer reactivity ratios and the experimental error are based upon the three analyses in each of runs 5a and 5c. The composition of the product of run 5b is not accurately known. In experiments 1–4, the spread in the three pairs of values of the monomer reactivity ratios is taken as the experimental error in the summary Table II.

Differences between experiments run at different times (and not recorded here) are in general of the same magnitude as the spread in a set of three runs in one experiment.

The Relative Reactivity of Monomers with Free Radicals.—The data in Table I and Fig. 1 are summarized in Table II; results on the styrene–methyl methacrylate system come from the previous paper.[2] In the copolymerizations of styrene with methyl methacrylate or with acrylonitrile, there is a tendency for the monomers to alternate in entering the copolymer, all the monomer reactivity ratios being less than one. In three of the other four pairs, one monomer reactivity ratio is greater than unity, the other less than unity, so that both radical types prefer to react with the same monomer. No copolymerization here described, however, is "ideal" according to the recent definition of Wall,[3] a necessary condition being that one monomer reactivity ratio be the reciprocal of the other. In no case described here will one constant adequately describe the products of copolymerization from a wide range of feed ratios.

Table II shows that the rate constant for the reaction of a styrene-type radical with methyl

TABLE II

MONOMER REACTIVITY RATIOS FOR SEVERAL MONOMER PAIRS[a]

Styrene	0.50 ± 0.02	Methyl methacrylate	0.50 ± 0.02
Styrene	0.41 ± 0.08	Acrylonitrile	0.04 ± 0.04
Styrene	2.00 ± 0.1	Vinylidene chloride	0.14 ± 0.05
Methyl methacrylate	1.20 ± 0.14	Acrylonitrile	0.15 ± 0.07
Methyl methacrylate	2.53 ± 0.1	Vinylidene chloride	0.24 ± 0.03
Acrylonitrile	0.91 ± 0.1	Vinylidene chloride	0.37 ± 0.1

[a] The number after each monomer is the monomer reactivity ratio of the corresponding radical-type in the copolymerization of the indicated pair of monomers.

methacrylate is just twice as large as the rate constant for its reaction with styrene; for its reaction with acrylonitrile, the constant is two and one-half times as large as for its reaction with styrene; and for its reaction with vinylidene chloride, the constant is one-half as large as for the reaction with styrene. Taking the rate constant for the reaction of a styrene-type radical with styrene as 1.00, and making the reasonable assumption[5] that it is independent of the reaction medium, the relative values of the rate constants for the reaction of the four monomers with the styrene-type radical are listed in Table III. The order of activity of the same monomers toward the three other radical types has been calculated similarly. Note, however, that a different (and at present not measurable) rate constant is taken as standard in each column and hence the absolute values in one column have no known relation to the absolute values in another column.

TABLE III

RELATIVE REACTIVITY OF MONOMERS WITH FOUR TYPES OF RADICALS[a]

Radical type Monomer	Styrene	Methyl meth-acrylate	Acrylo-nitrile	Vinyli-dene chloride
Styrene	1.00	2.0 (1.9–2.1)	25 (12–100)	7 (5–11)
Methyl meth-acrylate	2.0 (1.9–2.1)	1.00	7 (5–12)	4.1 (3.7–4.7)
Acrylonitrile	2.5 (2.0–3.0)	0.83 (0.75–0.95)	1.00	2.7 (2.1–3.7)
Vinylidene chloride	0.50 (0.47–0.53)	0.40 (0.38–0.41)	1.1 (1–1.2)	1.00

[a] The values given are the reciprocals of the corresponding monomer reactivity ratios in Table II. The ranges given in parentheses are the reciprocals of the estimated limits in that Table.

The data collected in Table III show clearly that the rates of reaction of free radicals with monomers are specific. Toward three kinds of radicals, the general order of decreasing monomer activity is that shown in the table, styrene being most reactive and vinylidene chloride being least reactive. However, styrene is only five times as reactive as vinylidene chloride with the methacrylate-type radical, but 23 times as reactive in the case of the acrylonitrile-type radical. On the other hand, the latter radical makes little or no distinction between acrylonitrile and vinylidene chloride, in comparison with the other two kinds of radicals. Finally, the order of activity of monomers with the styrene-type radical has no relation to the order with the other three radicals. Qualitatively, this work, together with more not yet published, suggests that there may be a general order of activity of monomers toward radicals which is complicated by the tendency of some pairs to alternate in copolymerization. This alternation effect seems sometimes to be due to steric effects, at other times, to dipole effects or specific interactions (compound formation) between monomers.

Rates of Polymerization and Copolymerization.—Table IV summarizes some information on initial rates of polymerization and copolymerization at 60°, expressed in weight per cent. per hour, in reaction mixtures containing 0.1 mole per cent. of benzoyl peroxide. With the exception noted, the rates were obtained from Table I by dividing yields by reaction times and are accurate enough for the present purpose.

TABLE IV

RATES OF POLYMERIZATION AND COPOLYMERIZATION AT 60°[a]

Polymerization of				
Acrylo-nitrile	Methyl meth-acrylate	Vinyli-dene chloride	Styrene	With
91[b]				Acrylonitrile
4.7	7.8[c]			Methyl methacrylate
4.9	3.9	3.3[b]		Vinylidene chloride
4.5	1.7[c]	1.14	1.6	Styrene

[a] Initial rates of polymerization in presence of 0.1 mole per cent. of benzoyl peroxide, expressed in weight per cent. per hour. In copolymerizations, the rates refer to equimolar mixtures. [b] Unpublished work by Mr. R. Van Meter; acrylonitrile polymerized to extent of 40% in 0.44 hour; vinylidene chloride, 3.3% in one hour. [c] From ref. 2.

Although styrene alone polymerizes slower than any of the other monomers, it enters the copolymers with acrylonitrile and vinylidene chloride relatively faster. Similarly, methyl methacrylate enters the copolymer faster than acrylonitrile, although the ester polymerizes slower alone than the nitrile. Although most of the combinations polymerize at a rate intermediate between the rates of polymerization of the monomers alone, the styrene–vinylidene chloride combination polymerizes significantly slower than either monomer alone. This case can be qualitatively

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(5) The rate constant for the uncatalyzed polymerization of styrene is nearly independent of the solvent employed; *cf.* Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937); Suess and Springer, *ibid.*, **A181**, 81 (1937); Schulz, Dinglinger and Husemann, *ibid.*, **B43**, 385 (1939).

interpreted on the basis that vinylidene chloride serves as a moderately unreactive diluent for the more reactive styrene and that the vinylidene chloride cannot polymerize by itself because the vinylidene chloride-type radicals are quickly converted to styrene-type radicals by their preferred reaction with styrene. However, there is no close relation between the rates of polymerization of two monomers by themselves and their relative tendencies to react with free radicals and enter a copolymer. Quantitative study of such relations (including those between the different standards in Table III) must await development of a method for measuring, estimating, or comparing very low concentrations of free radicals in solution.

Other Problems in Copolymerization.—The copolymerization equation is the most useful tool now available for comparing the behavior of monomers in copolymerizations. Its development assumed that the reactions of the growing radicals with monomers depend only on the monomer units which form the free radical ends of the growing chains and on the relative monomer concentrations. The usual small spread in monomer reactivity ratios over a wide range of feed ratios shows that these assumptions are excellent approximations, at least within experimental error. However, as our techniques have improved, we occasionally find instances where the discrepancy among the three pairs of solutions to three equations is beyond our expected experimental error. Some of these effects now seem to be associated with the size of the monomer unit adjacent to the terminal radical units in the growing chains, others with an actual or incipient precipitation of the polymer. Since the effects have become noticeable only with the most careful work, their investigation is difficult. Finally, the effects of temperature on some monomer reactivity ratios give some insight into the manner in which substituents affect reactivity. We have made substantial progress in investigating most of the problems mentioned and we hope to report some of our results in the near future.

Summary

The copolymerizations of acrylonitrile, methyl methacrylate, styrene and vinylidene chloride, taking two monomers at a time, have been studied at 60° with benzoyl peroxide as catalyst. The good correlation of the experimental data by the copolymerization equation which was previously developed indicates that the assumptions made about the chain growth process are substantially correct.

The relative reactivities of the four kinds of monomers with the four kinds of free radicals are compared. The results show clearly that reactions of free radicals with double bonds are specific, that both the ratio and the order of reactivities of a monomer series change as the radical is changed. There is no simple relation between the relative tendencies of two monomers to enter a copolymer and their rates of polymerization alone.

The copolymerization equation is a useful tool for pointing out and measuring the factors which govern copolymerization reactions. Investigation of several of these factors is in progress.

Difficulties in the analysis of certain polymers are discussed.

PASSAIC, NEW JERSEY RECEIVED JUNE 13, 1945

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES, RESEARCH AND DEVELOPMENT DEPARTMENT]

Physical Properties of Thiophene[1]

BY FRANK S. FAWCETT AND HERBERT E. RASMUSSEN

In a new process for the production of thiophene, a product has been obtained which has consistently had physical properties differing somewhat from data appearing in the literature. A consideration of the literature data summarized in Table I shows that, while the reported properties have been in general agreement from the time of the earliest observer, the properties of no one sample agree in all respects with a critical average of the data of the several investigators. The melting point especially is in doubt. With larger quantities than have previously been available, it seemed desirable to carry out extensive purification of thiophene and to redetermine its physical properties.

Purification of Thiophene

Four liters of the pilot plant product, obtained as a constant boiling distillate from a 15-theoretical plate column, was washed successively with dilute hydrochloric acid, sodium hydroxide, and distilled water and dried over calcium chloride. Approximately two liters was distilled at atmospheric pressure with a reflux ratio of 50:1 using a rectifying column having the following characteristics: rectifying section, 18 mm. i. d., 235 cm. length; packing, 2.4 mm. o. d. 1.25-turn helices of no. 30 B. & S. gage stainless steel wire; head, total condensation variable take-off; temperature measurement, 1-junction iron–constantan thermocouple with a Leeds and Northrup No. 8662 potentiometer. The product was collected as several fractions substantially all boil-

[1] Presented at the Spring Meeting, Philadelphia Section of the American Chemical Society, Philadelphia, June 13 1945.