PHYSICAL AND INORGANIC CHEMISTRY

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Kinetics of Anionic Polymerization and Copolymerization of the Vinylnaphthalenes and Styrene. The Intramolecular Charge-Transfer Complexes

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The absolute rate constants of anionic homopropagation of the 1- and 2-vinylnaphthalenes and of cross-propagation of living polystyrene with the vinylnaphthalenes were determined by the capillary-flow technique. In tetrahydrofuran at 25° the homopropagation rate constants are $\sim$500 l./mole sec. and $\sim$300 l./mole sec. for the 1- and 2-isomer, respectively, and the copropagation rate constant $k_{S-,N}^*$ is $\sim$8000 l./mole sec. for either 1- or 2-vinylnaphthalene. The addition of styrene to living polyvinylnaphthalene is more complex. Addition of a small excess of styrene results in a relatively slow reaction, described by eq. 3, in which a "complex" is formed. Its absorption maximum appears at λ_{max} 440 mμ, while the absorption maximum of living vinylnaphthalene is at λ_{max} 558 mμ and that of living styrene at λ_{max} 340 mμ. Using a stop-flow technique, k_1 was determined to be 29.9 l./mole sec. Addition of a larger excess of styrene permits the observation of the subsequent two reactions, namely, eq. 4 and 5. The kinetic scheme involving all three reactions was established by studying the process in a stirred-flow reactor and by a stop-flow technique. The kinetics in a stirred-flow reactor gives the product $k_i k_p$, while the ratio k_p/k_i was obtained from experiments performed by a stop-flow technique. Combining these results one gets the values k_i = 2.0 l./mole sec. and k_p = 625 l./mole sec. The complex formation was found to be reversible, the rate constant of its dissociation being 10^{-4} to 10^{-5} sec. $^{-1}$. Hence, the equilibrium constant of the complexing process is $\sim 10^3$ to 10^4 l./mole. In the absence of a large excess of styrene but in the presence of a small amount of living polystyrene the complex dissociates, *i.e.*

$$\text{CHCH}_2\text{CH(Ph)}^- + \text{[CH}_2\text{CH(Ph)]}_n\text{CH}_2\text{CH(Ph)}^- \longrightarrow$$

$$\text{CH}^- + \text{[CH}_2\text{CH(Ph)]}_{n+1}\text{CH}_2\text{CH(Ph)}^-$$

since the equilibrium constant for the process $(S)_{n-1}S^- + S \rightleftarrows (S)_nS^-$ (S denoting styrene) is higher than that of the complex formation. This reaction causes a slow change in the spectrum, *i.e.*, the 440 mμ band disappears and the 558 mμ band reappears. In the presence of a living or dead polyvinylnaphthalene the living polystyrene is "killed" by a still slower proton-transfer process

$$\text{CH} + \text{CH}_2\text{CH(Ph)}^- \longrightarrow \text{C} + \text{CH}_2\text{CH(Ph)}$$

The formation of the "complex" exemplifies an extreme case of penultimate unit effect. No "complex" is formed between naphthalene in solution and a living polystyrene, the gain in energy is not sufficient to overcome the loss of entropy. However, in

$$\text{C}-\text{CH}_2\bar{\text{C}}\text{H(Ph)}$$

the anion is bound to be in the vicinity of naphthalene moiety, and hence the complexing is possible.

Continuing our program of systematic studies of kinetics of anionic homo- and copropagations, we recently investigated the homopolymerization of the vinylnaphthalenes and their copolymerization with styrene. All these investigations were carried out in tetrahydrofuran at room temperature, Na$^+$ being the counter-ion.

The absolute rate constants of homo- and copropagations were determined by the capillary-flow technique described in previous papers.[1,2] Solutions of the investigated living polymer and the monomer were mixed at the entrance of the flow capillary. The reaction took place in the capillary and was interrupted after a fraction of a second by running the mixture into wet tetrahydrofuran. The residual concentration of monomer was determined and the rate constant calculated. The time of polymerization was varied from 0.06–0.2

(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).

Fig. 1.—Visible and ultraviolet spectra of living poly-1-vinyl-naphthalene in tetrahydrofuran before and after addition of a small amount of styrene.

sec. for the homopropagations and from 0.02–0.06 sec. for the copolymerizations of living polystyrene with the vinylnaphthalenes. The reaction between monomeric styrene and living vinylnaphthalene turned out to be rather complex, and the details are fully discussed in the last part of this paper.

Experimental

1-Vinylnaphthalene and styrene were acquired commercially, and a sample of 2-vinylnaphthalene was kindly given to us by Dr. A. Rembaum. 1-Vinylnaphthalene was fractionated under reduced pressure on a spinning-band column, dried on calcium hydride, and once more distilled on a high vacuum line into ampoules equipped with breakseals. The ampoules were then sealed off from the line and stored in a freezer until needed. The purity of 1-vinylnaphthalene was checked by v.p.c. and even in the best samples we detected a small amount ($\sim 2\%$) of 2-vinylnaphthalene. The presence of this isomer is, however, of no consequence for the determination of the respective rate constants, since both monomers show similar reactivities (see Tables I and II).

TABLE I

HOMOPOLYMERIZATION OF THE 1- AND 2-VINYLNAPHTHALENES IN TETRAHYDROFURAN

Counter-ion, Na$^+$; $T = 25°$

Run	[Living ends], moles/l. $\times 10^3$	[Monomer], moles/l. $\times 10^3$	Conv., %	k_p, l./mole sec.
		1-Vinylnaphthalene		
25	1.11	82.5	2.5–7	487(?)
10	1.87	54.5	7–13	622
9	2.17	2.60	10–20	856(?)
3	2.28	14.9	9–18	594
5	3.39	21.9	8–17	422
4	4.30	14.9	11–25	405
6	6.17	22.3	13–27	372
17[a]	2.59	1.7	13–24	808[a]
		2-Vinylnaphthalene		
23	1.10	8.0	10–80	297[b]
24	1.54	12.0	20–90	272[b]

[a] This experiment was performed with a polymer possessing one terminal vinylnaphthalene unit preceded by a segment of polystyrene. The experiment was planned to check the effect of penultimate group on the rate constant of homopropagation. [b] These experiments were carried out by a stop-flow technique measuring the decrease in the optical density of 2-vinylnaphthalene at λ_{max} 339 mμ.

2-Vinylnaphthalene was four times recrystallized from methanol and then distilled under high vacuum. The purity of the final material was checked by v.p.c. and only one peak was observed on the chromatogram. The m.p. was found to be 64–65°. The crystals were sealed in appropriate ampoules without exposing them to air. The purification of styrene and tetra-

TABLE II

ADDITION OF 1- OR 2-VINYLNAPHTHALENE TO LIVING POLYSTYRENE IN TETRAHYDROFURAN

Counter-ion, Na$^+$; $T = 25°$

Run	[$\sim$S$^-$], moles/l. $\times 10^3$	[Monomer], moles/l. $\times 10^3$	Conv., %	k_{12},[a] l./mole sec.
		1-Vinylnaphthalene		
7	2.20	1.33	34–51	8270
8	2.67	1.79	41–55	8250
1	2.75	2.43	62–77	7000
		2-Vinylnaphthalene		
12	1.84	1.39	39–46	9200
11	2.25	2.38	33–45	8450
13	3.78	1.43	52–69	7700

[a] $k_{1,2}$ was calculated from second-order equation $k = (1/t)(a - b)^{-1} \ln b(a - x)/a(b - x)$.

hydrofuran was described in previous papers (see, e.g., ref. 1 and 2).

Solutions of the living polystyrene were prepared by our standard method (see, e.g., ref. 1 and 2). Their concentrations were determined during the experiments by titration with methyl iodide. The solutions of living vinylnaphthalenes were prepared by adding vinylnaphthalene to a solution of living polystyrene. In most preparations the initial concentration of the respective monomer exceeded that of living polystyrene ends by a factor of about 10. The data reported in this paper show that the rate constant of addition of the first monomeric unit is about ten times higher than the rate constant of homopropagation of vinyl-naphthalene, and therefore this procedure converts all the polystyrene living ends into polyvinylnaphthalene living ends. In some experiments we used a polystyrene possessing only one terminal vinylnaphthalene$^-$ unit on each end. These polymers were prepared by our conventional flow technique, i.e., by mixing equivalent amounts of solutions of living polystyrene and vinyl-naphthalene[3] in THF and collecting the reacting mixture in a specially designed evacuated ampoule attached to the end of the flow capillary. After preparation, the ampoule was sealed off. The reliability of the conversion could be checked spectrophoto-metrically. Living poly-1-vinylnaphthalene shows an absorption maximum at 558 mμ (ϵ 6500), the absorption curve being shown in Fig. 1. It should be noticed that the optical density at 558 mμ happens to be identical with that at 340 mμ. At the latter wave length, the spectrum of living polystyrene exhibits a maximum corresponding to ϵ 1.2 $\times$ 10^4. Hence, the presence of any residual polystyrene is revealed by an increase in the optical density at 340 mμ with respect to that observed at 558 mμ. The equality of the optical densities at these two wave lengths was demonstrated for preparations containing a 10% excess as well as for those containing a tenfold excess of vinylnaphthalene.

The spectrum of living poly-2-vinylnaphthalene shows a sharp peak at λ_{max} 410 mμ (ϵ 9100). The solution is green, whereas that of poly-1-vinylnaphthalene is purple.

The concentrations of the residual vinylnaphthalenes in polymerized mixtures were usually determined spectrophotometrically. 1-Vinylnaphthalene in THF solution shows two absorption peaks at longer wave length; namely, λ_{max} 338 mμ (ϵ 85.4) and λ_{max} 331 (ϵ 592). The latter was used in determining the concentration in the reaction mixture, a solution of the polymer at the same concentration as that of the investigated solution being placed in the reference cell of the spectrophotometer. Calibration proved that this method is reliable if the polymer contains only a few vinylnaphthalene units per chain (naphthalene does not absorb at all at 330 mμ). Some determinations were accomplished by v.p.c. (using a hydrogen flame detector), but the spectrophotometric method was found to be quicker and more reproducible.

In determining the concentration of the residual 2-vinylnaphthalene in THF solution, we utilized the 339 mμ absorption peak of this monomer (ϵ 487). Its absorption spectrum shows two more peaks adjacent to the 339 one; namely, at λ_{max} 332 mμ (ϵ 406) and at λ_{max} 324 (ϵ 548). However, in determining the residual 2-vinylnaphthalene in its homopolymerization it was convenient to analyze the solution by v.p.c. using biphenyl as the internal standard.

The concentration of the residual styrene was determined by v.p.c. using a hydrogen flame detector and ethylbenzene as an internal standard.

Kinetics of Homopropagation of the Vinylnaphthalenes.—The results of the homopropagation of the 1- and 2-vinylnaphthalenes are given in Table I. The propagation rate constants, k_p, were calculated by plotting [living ends]$^{-1}$ ln $\{$[M]$_0$/[M]$_t\}$ vs. time

(3) To ensure a complete conversion of $\sim$S$^-$ ends into $\sim$vinylnaphthalene$^-$ ends, a slight excess ($\sim$10%) of monomer was added in the preparation.
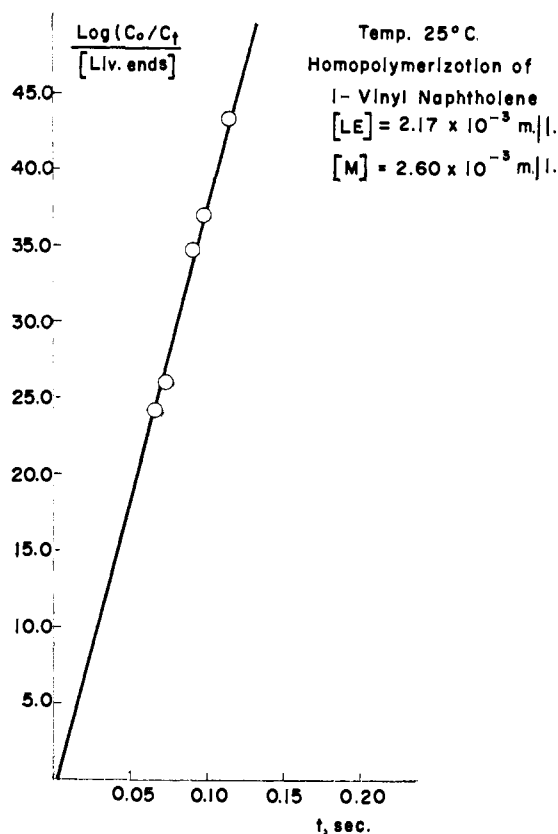
Fig. 2.—Kinetics of homopolymerization of 1-vinylnaphthalene. First-order plot of $\{\log (C_0/C_t)\}/[\text{Liv. ends}]$ vs. time. C_0 and C_t = the initial concentration of the monomer and its value at time t.

(i.e., assuming a plug flow and applying the first-order kinetic equation). The reproducibility of these experiments was good, as illustrated by a typical graph given in Fig. 2.

The experimentally determined values of k_p are similar to those found in the homopolymerization of styrene.[1] One should notice their decrease as the concentration of living ends increases, a common observation for most anionic polymerizations in tetrahydrofuran solution.[1,4] The cause of this phenomenon is still under investigation and will be discussed in a future communication.

In experiment 17 the penultimate unit was changed by substituting styrene for vinylnaphthalene. The effect of such a change is small in this system, although in some systems large effects were observed. For example, the rate constant of addition of 2-vinylpyridine to a living 2-vinylpyridine unit preceded by a styrene penultimate unit is about four times larger than the homopropagation rate constant of the ordinary living poly-2-vinylpyridine.[5]

Kinetics of Copolymerization of Living Polystyrene with the Vinylnaphthalenes.—The results of copolymerization studies of living styrene with the vinylnaphthalenes are given in Table II. The cross-propagation rate constants, k_{12}, are about 10 times greater than those for homopolymerization, and hence for the ratio $[\text{Monomer}]_0/[\sim S^-]_0 < 1$, the addition of the second unit of vinylnaphthalene to the growing polymer is negligible. Consequently, the respective rate constants were derived on the basis of a second-order equation (see ref. 2), i.e., by plotting $(a - b)^{-1}$ $\ln b(a - x)/a(b - x)$ vs. time. In this expression a and b denote the initial concentrations of living polystyrene and monomer; x represents the amount of polymerized monomer and t the time of reaction. The reproducibility of the results was again satisfactory, as demonstrated by typical graphs shown in Fig. 3. The observed values of k_{12}'s decreases slightly with the increasing concentration of living ends.

Discussion of Homopolymerization of the Vinylnaphthalenes and of their Copolymerization with Living Polystyrene.—The lower localization energies of the vinylnaphthalenes compared with styrene make the

(4) M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, J. Am. Chem. Soc., **85**, 1306 (1963).

(5) C. L. Lee, J. Smid, and M. Szwarc, Trans. Faraday Soc., **59**, 1192 (1963).
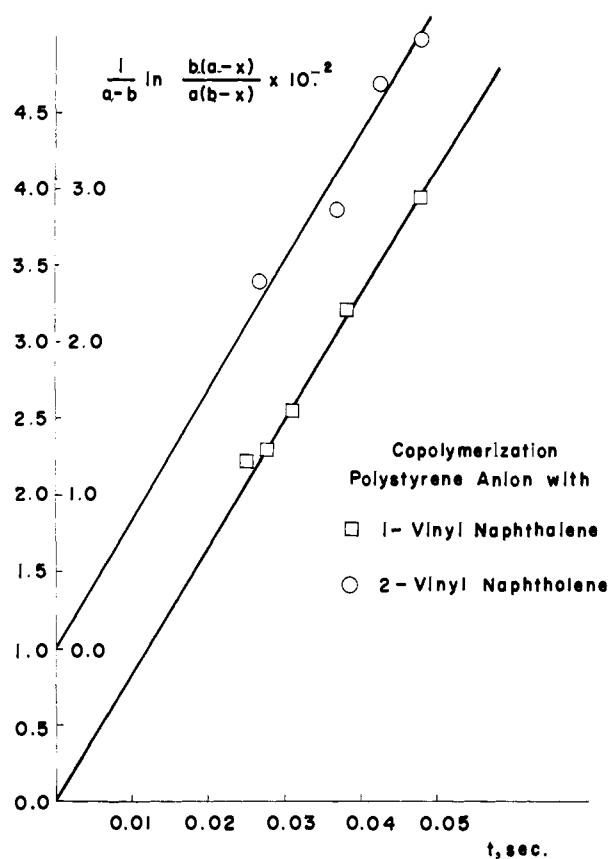
Fig. 3.—Kinetics of copolymerization of 1- and 2-vinylnaphthalenes with living polystyrene. The monomer concentration was lower than that of living ends. The reaction obeys second-order kinetics. The line for 2-vinylnaphthalene was shifted by one unit upward.

former monomers more reactive than the latter. The observed difference in reactivities toward methyl radical addition is small[6]; i.e., at 65° k_2/k_1 = 813 ± 25 for 1-vinylnaphthalene and 792 ± 26 for styrene. In respect to polystyryl radical, which is more selective than methyl radical, 2-vinylnaphthalene is twice as reactive as styrene[7] (r_1 and r_2 determined at 60°); however, it is only 1.4 times as reactive as styrene in respect to polyvinylnaphthalene radical.[7]

It is interesting to notice how the reactivities of 2-vinylnaphthalene and 2-vinylpyridine differ in a radical and in anionic polymerization. In respect to polystyryl radical, 2-vinylnaphthalene is slightly more reactive than 2-vinylpyridine, the order of reactivities essentially reflecting the resonance stabilization of the monomer and the radical. In respect to polystyryl anion, 2-vinylpyridine is more than ten times as reactive as 2-vinylnaphthalene (see ref. 5). Obviously these results indicate a much greater electron affinity of the pyridine ring than that of naphthalene. This conclusion is supported by studies of the penultimate effects. It is believed[5] that the presence of a pyridine ring in the penultimate unit reduces by virtue of its high electron affinity the reactivity of living polyvinylpyridine. This effect disappears when styrene replaces vinylpyridine in the penultimate unit, and consequently such a polymer adds vinylpyridine four or five times faster than the ordinary living polyvinylpyridine. Since the electron affinity of naphthalene moiety is not as great as that of pyridine, replacement of naphthyl

(6) F. Carrock and M. Szwarc, J. Am. Chem. Soc., **81**, 4138 (1959).

(7) C. C. Price, B. D. Halpern, and S. T. Boong, J. Polymer Sci., **11**, 575 (1953); see also for the recalculated Q's and e's, T. C. Schwan and C. C. Price, ibid., **40**, 457 (1959).
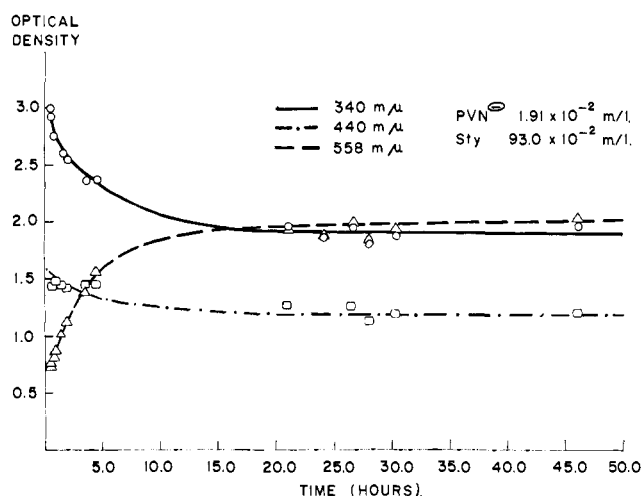
OPTICAL
DENSITY

Fig. 4.—The changes in the optical densities of a solution of living polyvinylnaphthalene after addition of a large excess of styrene.

moiety in the penultimate unit by phenyl leads only to a small effect (see Table I, expt. 17).

The differences in k_{12}, ($\sim$S⁻ + VN), and k_{11}, ($\sim$S⁻ + S), are not reflected in the respective homopropagations, i.e., in the processes $\sim$(VN)⁻ + VN and $\sim$S⁻ + S. One would expect the former reaction to be faster than the latter; however, steric strain may be responsible for the observed results, as is indeed indicated by the inequality $1/r_1 > r_2$ (see ref. 7).

Finally, we should mention some results obtained by Natta and his colleagues.[8] These workers investigated the copolymerization of styrene with other aromatic vinyl compounds using the Ziegler–Natta heterogeneous catalysts (TiCl₄ + AlEt₃ at 60°). The reactivity ratios, r_1 and r_2, were obtained by the conventional method based on the analysis of the copolymer composition as a function of feed composition. The analytical problems were solved by using monomers labeled with C¹⁴.

Results of their work are discussed in terms of steric and polar effects. The process seems to be favored by a high electron density on the C=C bond, i.e., the coordination of the monomer with the catalyst appears to be the rate-determining step in this copolymerization (the vacant d-orbital of the catalyst acts as the acceptor of π-electrons of the monomer).

The copolymerization of styrene with the vinylnaphthalenes behaved "ideally," i.e., the product r_1r_2 was unity.

Spectrophotometric Studies of Copolymerization of Styrene with Living Vinylnaphthalene.—When styrene is added to living 1-vinylnaphthalene, peculiar changes occur in the absorption spectrum of the solution. A few seconds after addition of a small excess of styrene, the characteristic absorption peak of living poly-1-vinylnaphthalene (λ_{max} 558 mμ; see curve A in Fig. 1) disappears, and a new peak appears at λ_{max} 440 mμ (see curve B in Fig. 1). The anticipated absorption peak at λ_{max} 340 mμ, characteristic of living polystyrene, is not developed. Within 24 hr., the original absorption spectrum of living polyvinylnaphthalene reappears (see curve C in Fig. 1), although its intensity is lower. The decrease in the intensity was accounted for by dilution and perhaps by some killing.

However, the addition of a large, e.g., a 50-fold, excess of styrene converts the absorption spectrum of the solution from that characteristic of living poly-1-vinylnaphthalene (λ_{max} 558 mμ) to the one observed for

(8) G. Natta, et al., Chim. Ind. (Milan), **41**. 964, 968, 1176 (1959).

a solution of living polystyrene (λ_{max} 340 mμ). This spectrum also is converted in about 15–20 hr., into that of living poly-1-vinylnaphthalene. These changes are presented graphically in Fig. 4. It has been shown that the relation, [o.d.(340)]/[o.d.(558)] = 1 is characteristic for the absorption spectrum of living poly-1-vinylnaphthalene. Therefore, it is significant that the ratio of optical densities at 558 mμ and at 340 mμ (triangles and circles, respectively) approach unity after about 20 hr. It is also significant that the absorption maximum at 440 mμ does not appear in these experiments.

We conclude, therefore, that addition of a large excess of styrene to living poly-1-vinylnaphthalene leads to polymerization and eventually to the formation of ordinary styrene⁻ ends, i.e.

$$\sim\text{CH}_2\text{CH}^- + n\text{S} \rightarrow \sim\text{CH}_2\text{CHSS} \sim\text{SS}^- \quad (1)$$
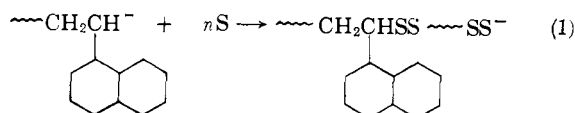
Since the hydrogens on carbons α to the naphthalene rings are more acidic than benzylic hydrogens, the living polystyrene ends, $\sim$CH₂CH(Ph)⁻, are expected slowly to acquire protons from the segments of polyvinylnaphthalene, i.e.

$$\sim\text{CH}_2\text{CH}\sim + {}^-\text{CH(Ph)}\sim \rightarrow \quad (2)$$
$$\sim\text{CH}_2\bar{\text{C}}\sim + \text{CH}_2(\text{Ph})\sim$$
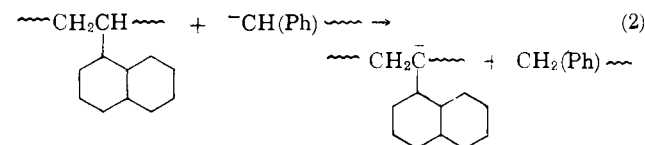
This plausible reaction accounts for the reappearance of the spectrum of living vinylnaphthalene.

To prove the feasibility of the proton-transfer reaction, we performed the series of experiments described in Table III. In the first series, a solution of

TABLE III

REACTION OF LIVING POLYSTYRENE WITH
POLY-1-VINYLNAPHTHALENE IN THF AT ROOM TEMPERATURE

t, hr.	O.d., 340 mμ	O.d., 558 mμ
Living polystyrene + dead poly-1-vinylnaphthalene		
0	0.74	0.066
0.15	.70	.095
3.0	.49	.182
21.0	.33	.280
28.0	.32	.290
Living polystyrene + living poly-1-vinylnaphthalene		
0	1.29	0.54
0.1	1.18	.57
1.0	1.08	.72
19.0	0.81(?)	.91
90.0	0.89	.91
Living polystyrene + α-methylnaphthalene		
0.20	0.500	0.094ᵃ
.25	.492	.113ᵃ
.50	.375	.176ᵃ
1.50	.304	.232ᵃ
19.0	.263	.250ᵃ
43.0	.261	.269ᵃ

ᵃ Measured at the respective absorption peak of 540 mμ.

living polystyrene was allowed to react with a solution of dead polyvinylnaphthalene. The latter polymer was obtained from a living poly-1-vinylnaphthalene by killing with water. Its solution in THF was thoroughly dried and deaerated before performing the experiment. The results definitely show that proton transfer takes place, the reaction approaching completion in about

Table IV

⁓⁓S…S(VN)⁻, Na⁺ + styrene; solvent − THF, T = 25°

Run 1	Description of operation	O.D., 340 mμ	O.D., 440 mμ	O.D., 558 mμ
1	Spectrum of polystyrene containing ∼1.5 vinyl naphthalene units per end [LE] = 16 × 10⁻³ M. See curve A, Fig. 1	Obs. *1.77*	Obs. *0.98*	Obs. *1.75* max.
2	Styrene added in 1.5 excess of living ends. [LE] = 11.6 × 10⁻³ M. See curve B. Fig. 1	Obs. *1.19*	Obs. *1.19* max.	Obs. *0.54* plat.
	Calcd. from 1 on the basis of diln.	1.28	0.71	1.27 max.
	Calcd. on the assumption that all the ends are converted into ⁓⁓S⁻	2.36 max.	..	..
3	After standing for 24 hr. See curve C, Fig. 1	Obs. *1.33*	Obs. *0.72*	Obs. *1.18* max.
4	Styrene added in 2.0 excess of living ends. [LE] = 9.1 × 10⁻³ M	Obs. *0.90*	Obs. *0.90* max.	Obs. *0.37* plat.
	Calcd. from 3 on the basis of diln.	1.04	0.57	0.93 max.
	Calcd. on the assumption that all the ends are converted into ⁓⁓S⁻	1.73 max.	..	..
5	After standing for 24 hr.	Obs. *1.03*	Obs. *0.54*	Obs. *0.85* max.
6	Styrene added in 2.4 excess of living ends. [LE] = 7.5 × 10⁻³ M	Obs. *0.72*	Obs. *0.71* max.	Obs. *0.25* plat.
	Calcd. from 5 on the basis of diln.	0.86	0.44	0.70 max.
	Calcd. on the assumption that all the ends are converted into ⁓⁓S⁻	1.30 max.		
7	After standing for 24 hr.	Obs. *0.80*	Obs. *0.40*	Obs. *0.63* max.
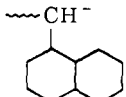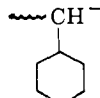
20 hr. The reaction of living polystyrene with living poly-1-vinylnaphthalene was investigated in turn, and the results prove that a proton may be transferred even from middle segments of the polymer. Finally, the last series of experiments was performed with α-methylnaphthalene as the proton donor, and the results again confirmed the feasibility of proton transfer. The last reaction was faster than the previous one, since the concentration of α-methylnaphthalene was relatively high. In addition, this experiment demonstrated that the spectrum of α-$C_{10}H_7CH_2^-$ ions is not markedly different from that of α-$C_{10}H_7CH^-CH_2$⁓⁓, and therefore one anticipates the spectrum of the α-$C_{10}H_7C^-$-$(CH_2$⁓⁓$)_2$ ions to be similar to that of living poly-α-vinylnaphthalene ends.

As mentioned earlier a new band at λ_{max} 440 mμ appears after the addition of a small excess of styrene to living poly-1-vinylnaphthalene. This band may be due to an intermediate formed on the addition of the first styrene molecule to living vinylnaphthalene. In the presence of a large excess of styrene, this intermediate reacts further and eventually forms long chains of styrene units with a terminal S⁻. This conclusion follows from the observation that no absorption maximum at λ 440 mμ is observed on the addition of a large excess of styrene.

To gain more information about the nature of this intermediate and the mechanisms by which it forms the

⁓⁓C⁼⁼
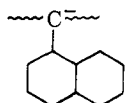
units, we performed the experiments described in Table IV. The living polymer used in the studies was prepared from living polystyrene to which ∼50% excess of 1-vinylnaphthalene was added. The absorption spectrum of the solution was typical of living poly-1-vinylnaphthalene, λ_{max} 558 mμ, and the optical densities at 558 and 340 mμ were 1.75 and 1.77, respectively. On addition of 1.5 equivalents of styrene, the optical densities at 558 and 340 mμ were reduced to 0.54 and 1.19, and the new maximum, developed at 440 mμ, showed an optical density of 1.19 (see Table IV). The effect of dilution, caused by the addition of styrene, should reduce the optical densities at 340, 440, and 558 mμ to 1.28, 0.71, and 1.27, respectively. Had the

⁓⁓CH⁻

addition of styrene converted the [structure] ends into
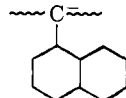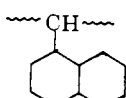
⁓⁓CH⁻

ends, the anticipated spectrum would show

a single maximum at 340 mμ with an optical density of 2.36.

After 24 hr., the spectrum of the solution had changed. The usual absorption of living poly-1-vinylnaphthalene was recorded and the observed optical densities were 1.33 (λ 340 mμ), 0.72 (λ 440 mμ), and 1.18 (λ 558 mμ). It is significant that the optical density at 340 mμ was slightly higher, and that at 558 mμ slightly lower than those calculated on the basis of dilution (see Table IV). This seems to indicate that some ordinary living polystyrene ends were eventually formed in the reaction, and in the period of 24 hr. not all of them acquired protons from the vinylnaphthalene segments, since in this experiment the concentration of the available protons was low.
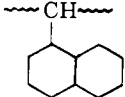
Addition of a new portion of styrene (∼2 equivalents) again produced the intermediate, its optical density being 0.90 at λ_{max} 440 mμ, and the optical densities at 558 and 340 mμ decreased to values lower than anticipated on the basis of dilution (see Table IV). However, the spectrum of living polyvinylnaphthalene again reappeared after 24 hr., and significantly the relative concentration of residual living polystyrene ends slightly increased.

The addition of a third portion of styrene again reproduced the described cycle of events (see Table IV).

It was pointed out earlier that the conversion of the

⁓⁓C⁼⁼

ordinary living polystyrene ends into [structure] units

⁓CH⁓

involves proton transfer from the [structure] groups.

However, had each intermediate, formed after styrene addition, acquired a proton to produce the observed change, the third, and perhaps even the second, repetition of the cycle would be impossible in view of the

⁓⁓CH⁓

limiting amount of the [structure] groups initially

present in the original solution. Hence, it is obvious that the conversion of the intermediates into living polyvinylnaphthalene must proceed through a different path from that outlined for the conversion of ordinary living polystyrenes into living polyvinylnaphthalenes.

The following mechanism is proposed to account for these facts, and its justification will be presented later in the paper. We suggest that the addition of the first
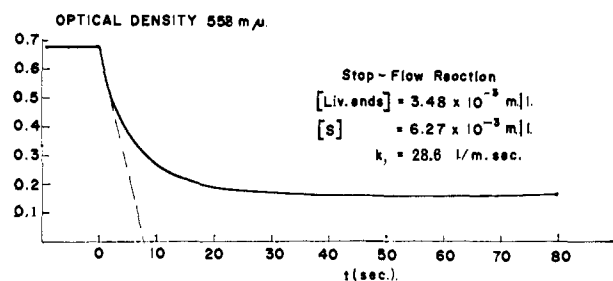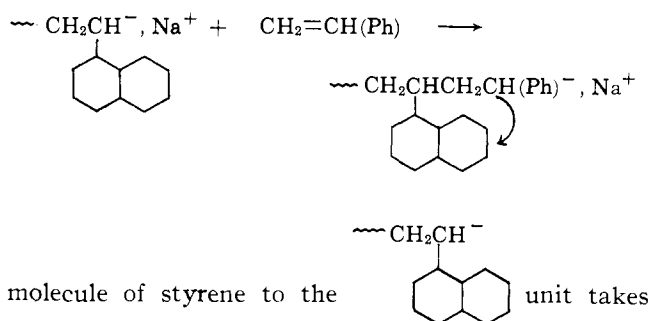
Fig. 5.—Change in the optical density at 558 mμ observed in a stop-flow technique for the reaction

$$\sim CH_2CH^-, Na^+ + CH_2{=}CH(Ph) \longrightarrow$$

$$\sim CH_2CHCH_2CH(Ph)^-, Na^+$$
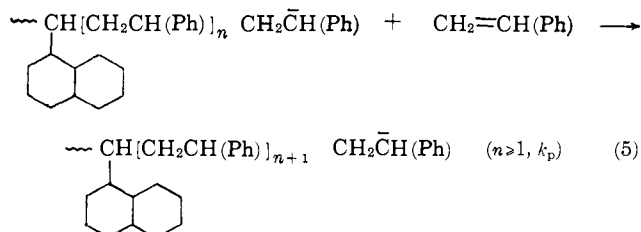
molecule of styrene to the ⟨unit⟩ unit takes place rapidly (within a few seconds) and produces a covalently bonded styrene⁻ unit associated, by virtue of charge-transfer forces, with the preceding naphthalene moiety. This may be described by the equation,
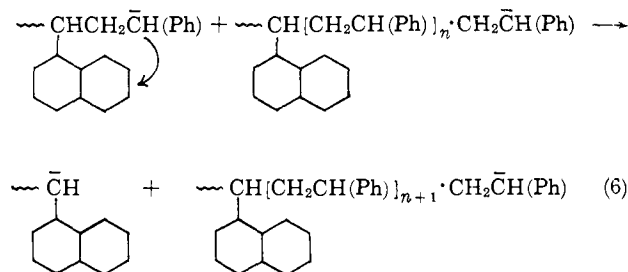
$$\sim CH^- + CH_2{=}CH(Ph) \rightleftarrows \sim CHCH_2\bar{C}H(Ph) \qquad (3)$$
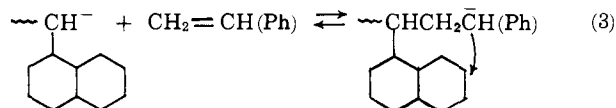
where the curved arrow symbolizes the charge-transfer interaction between $\sim\bar{C}H(Ph)$ and the naphthalene residue. We suggest that the observed absorption spectrum corresponding to λ_{max} 440 mμ arises from this interaction and that the resulting complex is relatively inert with respect to polymerization. Therefore, the addition of a second molecule of styrene

$$\sim CHCH_2\bar{C}H(Ph) \xrightarrow{+\ CH_2{=}CH(Ph)} \sim CHCH_2CH(Ph)CH_2\bar{C}H(Ph) \quad k_j \qquad (4)$$
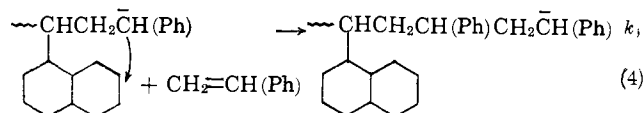
proceeds slowly. This reaction produces ordinary, non-associated terminal styrene⁻ units and further addition of styrene molecules to these units takes place by the conventional, rapid propagation process with a rate constant k_p characteristic of living polystyrene polymerization, i.e.

$$\sim CH[CH_2CH(Ph)]_n\ CH_2\bar{C}H(Ph) + CH_2{=}CH(Ph) \longrightarrow$$

$$\sim CH[CH_2CH(Ph)]_{n+1}\ CH_2\bar{C}H(Ph) \quad (n{\geqslant}1,\ k_p) \qquad (5)$$

where $k_p \gg k_1$. The concentration of styrene in equilibrium with living polystyrene is apparently much lower than for the reversible addition of the first styrene molecule to the living vinylnaphthalene unit. Hence, on addition of a small excess of styrene to living vinylnaphthalene, essentially all the vinylnaphthalene units add one styrene molecule, while few of them will possess two or more styrene units. The reversibility of the first addition leads then to a slow reaction

$$\sim CHCH_2\bar{C}H(Ph) + \sim CH[CH_2CH(Ph)]_n{\cdot}CH_2\bar{C}H(Ph) \longrightarrow$$

$$\sim \bar{C}H \quad + \quad \sim CH[CH_2CH(Ph)]_{n+1}{\cdot}CH_2\bar{C}H(Ph) \qquad (6)$$

which converts the complex into living polyvinylnaphthalene and leaves a relatively small fraction of living polymers in the form of living polystyrene. Superimposed on this reaction is an even slower proton-transfer process terminating the living polystyrenes and regenerating the $\sim\bar{C}$(naphthyl)$\sim$ units in the chain. It is most probable that the complexed styrene units do not acquire protons from the $\sim CH$(naphthyl)$\sim$ groups, since their basicity, when compared to that of the ordinary living polystyrene, is greatly reduced by the charge-transfer interaction. Thus, relatively few polymeric ends containing terminal styrene⁻ units acquire protons through reaction 2, while most of them lose their single styrene molecules through reaction 6. This explains the results given in Table IV, i.e., why the reappearance of the living vinylnaphthalene spectrum may be observed several times in spite of the fact that the total initial concentration of vinylnaphthalene units is approximately equal to the concentration of living ends.

Kinetics of Styrene Addition to Living Polyvinylnaphthalene.—The mechanism proposed in the preceding section was confirmed by kinetic studies. The first step of the reaction

$$\sim CH_2CH^- + CH_2{=}CH(Ph) \longrightarrow \sim CH_2CHCH_2CH^-(Ph) \quad k_1$$
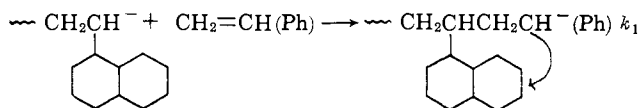
was investigated by the stop-flow technique described previously.[9] A solution of living polyvinylnaphthalene in tetrahydrofuran was mixed in a flow system with a solution of styrene and the mixture was flowed through an optical cell placed in a recording spectrophotometer. In these experiments the solution reached the cell about 0.2 sec. after mixing the reagents. The spectrophotometer was set on 558 mμ (the λ_{max} of living polyvinylnaphthalene) or on 440 mμ (the λ_{max} of the complex). After a few seconds the flow was stopped and the progress of the reaction followed by recording the decrease in the optical density at 558 mμ or its increase at 440 mμ. A typical tracing of the recorder is shown in Fig. 5.

The initial rate of the reaction was determined from the initial slope of the descending curve at 558 mμ, and the initial concentration of living ends from the optical density of the solution observed at the same wave length during the flow. This procedure leads to a correct result, even if there is some initial killing of living ends owing to impurities present in the monomer solution. The concentration of styrene was calculated from the known concentration of the stock solution and the dilution factor determined by the rates of flow of both liquids.

Let ϵ_1 and ϵ_2 be the extinction coefficients of living vinylnaphthalene and the complex at 558 mμ. The coefficient ϵ_1 is determined directly. To determine ϵ_2 we have to convert quantitatively a solution of living vinylnaphthalene into the complex. The data given

(9) J. Jagur, M. Levy, M. Feld. and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2168 (1962).

in Table IV show that on addition of a slight excess of styrene to living vinylnaphthalene, the optical density at 558 mμ falls to about 0.4 of its initial value (correcting for the dilution factor). Hence, $\epsilon_2/\epsilon_1 < 0.4$ since it is probable that under these conditions the conversion was not quantitative. From the experiments in the flow system it was found that the ratio of final and initial optical densities at 558 mμ were 0.1 for $[S]_0/[liv. ends]_0 > 12$. It is probable that some complex units were converted into living polystyrene when the ratio $[S]_0/[liv. ends]_0 > 12$, and this could decrease the optical density at 558 mμ. In fact, the general appearance of the final spectrum observed in such experiments supports this assertion. Hence, $\epsilon_2/\epsilon_1 > 0.1$. On the other hand, the final spectra, observed in the flow experiments in which $[S]_0/[liv. ends]_0$ varied from 1.5 to 4, gave a constant value for the ratio of initial and final optical densities at 558 mμ, namely

$$0.245 \text{ for } [S]_0/[LE]_0 = 3.87$$
$$0.279 \text{ for } [S]_0/[LE]_0 = 3.12$$
$$0.281 \text{ for } [S]_0/[LE]_0 = 3.35$$
$$0.270 \text{ for } [S]_0/[LE]_0 = 1.66$$
$$0.286 \text{ for } [S]_0/[LE]_0 = 1.52$$
$$0.238 \text{ for } [S]_0/[LE]_0 = 1.80$$

Moreover, the shape of these spectra indicated the absence of living polystyrene. Therefore the average value $\epsilon_2/\epsilon_1 = 0.27$ appears to be the most reliable and has been chosen for our calculations. On this basis the bimolecular rate constant k_1 was calculated from the equation

$$\{-\text{d(o.d. at 558)}/\text{d}t\}_0 = k_1\{(\text{o.d. at 558})\}_0[S]_0(1 - \epsilon_2/\epsilon_1)$$

where $1 - \epsilon_2/\epsilon_1 = 0.73$. The results are given in Table V and their consistency is gratifying. Notice that $1 - \epsilon_2/\epsilon_1$ is less affected by the uncertainty in ϵ_2/ϵ_1 than is the ratio itself.

TABLE V

REACTION OF LIVING POLYVINYLNAPHTHALENE
WITH STYRENE IN THF

Na$^+$, counter-ion; $T = 25°$; stop-flow technique

[Liv. ends]$_0$, moles/l. $\times 10^3$	[S]$_0$, moles/l. $\times 10^3$	[S]$_0$/[liv. ends]$_0$	O.d. at 558 mμ, init.	$-\left[\dfrac{\text{d(o.d. 558)}}{\text{d}t}\right]_0$	k_1, l./mole sec.
3.93	0.92	0.23	0.767	0.0146	28.5
3.56	1.11	.31	.694	.0178	31.6
(1) 3.39	1.21	.36	.660	.0180	31.0
3.32	1.24	.37	.648	.0185	31.6
3.27	1.25	.38	.638	.0184	31.6
3.79	6.31	1.66	.740	.0978	28.7
(2) 3.49	6.27	1.80	.681	.0895	28.6
(3) 4.77	18.46	3.87	.930	.370	29.6
4.41	65.20	14.80	.860	1.200	29.3
4.11	72.5	17.64	.800	1.222	28.7

Av. 29.9 ± 1.2

Alternatively, k_1 may be calculated from the data obtained at 440 mμ. However, we prefer to use these data to check the stoichiometry of the reaction by demonstrating the equality $-\text{d[liv. ends]}/\text{d}t = \text{d[complex]}/\text{d}t$.

If ϵ_1' and ϵ_2' denote the extinction coefficients of the living polyvinylnaphthalene and the complex at 440 mμ, then the stoichiometry of the reaction demands the ratio

$$\{[\text{d(o.d. 440)}/\text{d}t]_0/[\text{d(o.d. 558)}/\text{d}t]_0\} \{(\text{o.d. 558})_0[S]_0/(\text{o.d.}$$
$$558)_0'[S]_0'\} = (\epsilon_2' - \epsilon_1')/(\epsilon_2 - \epsilon_1)$$

to be constant. The pertinent results are given in Table VI, and to minimize the experimental errors, we combined in calculations the results of Table VI with those having the corresponding numbers in Table V. The consistency of the ratio $(\epsilon_2' - \epsilon_1')/(\epsilon_2 - \epsilon_1)$ proves the 1:1 stoichiometry of this reaction.

TABLE VI

TEST FOR THE STOICHIOMETRY OF THE COMPLEX FORMATION
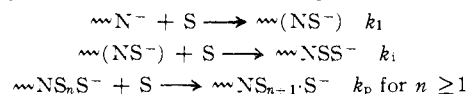
$T = 25°$; solvent, THF; Na$^+$, counter-ion

[Liv. ends]$_0$, moles/l. $\times 10^3$	[S$_0$]', moles/l. $\times 10^3$	O.d. at 558 mμ, init.	$\left[\dfrac{\text{d(o.d. 440)}}{\text{d}t}\right]_0$	$-\dfrac{\epsilon_2' - \epsilon_1'}{\epsilon_2 - \epsilon_1}^a$
(1) 3.33	1.20	0.650	0.0114	0.65
(2) 3.98	5.94	.777	.075	.77
(2) 3.90	5.94	.761	.073	.77
(3) 5.12	15.96	1.000	.226	.66

Av. 0.71 ± 0.06

^{a} $\dfrac{\epsilon_2' - \epsilon_1'}{\epsilon_2 - \epsilon_1} = \left\{\left[\dfrac{\text{d(o.d. 440)}}{\text{d}t}\right]_0/\left[\dfrac{\text{d(o.d. 558)}}{\text{d}t}\right]_0\right\} \times \{(\text{o.d.}$ $558)_0[S]_0/(\text{o.d. }558)_0'[S_0]'\}$. In calculation the runs denoted by (1), (2), and (3) were compared with the respective numbers of Table V.

From the spectrum of living polyvinylnaphthalene the ratio ϵ_1'/ϵ_1 was determined to be 0.47, and we accepted again the value of 0.27 as the best estimate for ϵ_2/ϵ_1. Hence, from the average value $(\epsilon_2' - \epsilon_1')/(\epsilon_1 - \epsilon_2) = 0.71$, we calculate $\epsilon_2'/\epsilon_1 = 0.99$, i.e., at λ_{max} 440 mμ the extinction coefficient of the complex is $\sim$6440.

Further steps of the reaction were investigated by means of a stirred-flow reactor. This reactor, described in an earlier paper,[10] is composed of an all-glass sealed cylinder with capillary inlets and outlet tubes, and of a cylindrical, magnetically driven glass rotor. The solutions of the living polymer and the monomer were flowed into the reactor from calibrated storage vessels (see, e.g., ref. 1) and the outlet capillary led the reacting mixture into wet tetrahydrofuran where the polymerization was instantly quenched. The concentration of the residual styrene was then determined. Two reactors were used: one of $\sim$6-cc. volume operating at residence time 2–17 sec., the other of about 8-cc. volume and performing at residence times from 6–26 sec. The rotors turned at $\sim$20 revolutions per second, i.e., the reacting mixture was turned over at least 40 times during the shortest residence time.

Our system is described by the equations

$$\text{\textasciitilde N}^- + S \longrightarrow \text{\textasciitilde}(NS^-) \quad k_1$$
$$\text{\textasciitilde}(NS^-) + S \longrightarrow \text{\textasciitilde}NSS^- \quad k_i$$
$$\text{\textasciitilde}NS_nS^- + S \longrightarrow \text{\textasciitilde}NS_{n+1}S^- \quad k_p \text{ for } n \geq 1$$

where $\text{\textasciitilde N}^-$ denotes a living polyvinylnaphthalene, $\text{\textasciitilde}(NS^-)$ the complex formed by the first added styrene unit with the preceding naphthyl group, and $\text{\textasciitilde}NS_nS^-$ for $n \geq 1$ an ordinary living polystyryl end. The following symbols will be used in the subsequent equations: $[\text{\textasciitilde N}^-] = x$, $[\text{\textasciitilde}(NS^-)] = C$, $[\text{\textasciitilde}NS_nS^-] = y$, and $[S] = S$. The balance equations of the stirred-flow reactor acquire the forms

$$\{k_1x + k_iC + k_py\}St = S_0 - S \qquad (a)$$
$$k_1xSt = x_0 - x \qquad (b)$$
$$\{k_1x - k_iC\}St = C \qquad (c)$$
$$k_iCSt = y \qquad (d)$$

where t is the residence time in the reactor, $t = $ (volume of the reactor)/(rate of flow). This set of equations leads to the relations

$$(S_0 - S - C - 2y)/CS^2 = k_ik_pt^2 \qquad (e)$$
$$C = k_1St(x_0 - y)/\{1 + (k_1 + k_i)St\} \qquad (f)$$

Hence, a plot of $(S_0 - S - C - 2y)/CS^2$ vs. t^2 should give a straight line with a slope equal to k_ik_p.

The application of this equation requires a series of successive approximations. The rate constant k_1 was determined by the stop-flow technique to be 29.9 l./

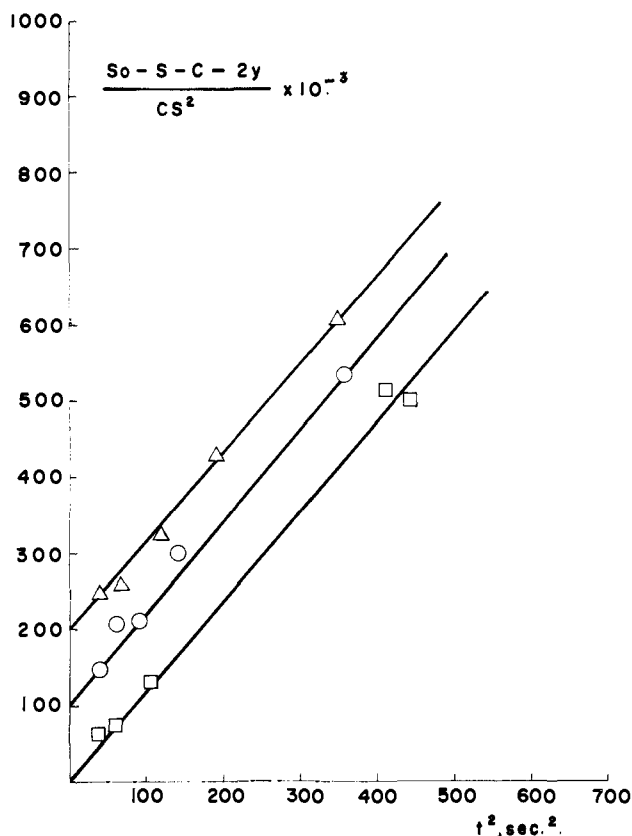(10) C. L. Lee, J. Smid, and M. Szwarc, J. Am. Chem. Soc., 85, 912 (1963).

Fig. 6.—Kinetics in the stirred-flow reactor. Plot of $(S_0 - S - C - 2y)/CS^2$ vs. t^2. The successive lines are shifted upward by 100 and 200 units, respectively. □, run 18, $(\sim N^-)_0 = 2.7 \times 10^{-3} M$, $[S]_0 = 4.5 \times 10^{-3} M$, $k_i k_p = 1260$; O, run 19, $[\sim N^-]_0 = 2.6 \times 10^{-3} M$; $[S]_0 = 11.5 \times 10^{-3} M$, $k_i k_p = 1160$; △, run 20, $[\sim N^-]_0 = 3.5 \times 10^{-3} M$, $[S]_0 = 54 \times 10^{-3} M$, $k_i k_p = 1160$.

mole sec. The rate constant k_p is known from the direct study of homopolymerization of living polystyrene,[1] and under the experimental conditions prevailing in the stirred-flow reactor, its value is ~600 l./mole sec. For a large value S_0–S the term y may be omitted in eq. e and in the first approximation C may be identified with x_0. In this way an approximate value of $k_i k_p \sim 1000$ is obtained from the plot

$$(S_0 - S - x_0)/x_0 S^2 \text{ vs. } t^2$$

Hence, $k_i > 1.6$, and an *a posteriori* justification leads to $k_i = 2.0$ l./mole sec. On the basis of $k_i = 2.0$ l./mole sec., we calculate C from the exact eq. f taking $y = 0$, and then calculate y from eq. d. This value is inserted into eq. f and a better approximation is obtained for C leading to a new value of y. Repetitions of these operations give eventually the correct values of C and y, which are used in turn to determine the function $(S_0 - S - C - 2y)/CS^2$. Plots of this function vs. t^2 for various initial values of S_0/x_0 are shown in Fig. 6 and 7. The required data are given in Table VII and the resulting values of $k_i k_p$ in Table VIII. The average value of $k_i k_p = 1230$ (l./mole)^2 sec.$^{-2}$ in conjunction with $k_p = 600$ l./mole sec. gives $k_2 = 2.05$ l./mole sec. This is therefore the *a posteriori* justification for choosing the value $k_i = 2.0$ l./mole sec. for our calculations.

The linearity of plots shown in Fig. 6 and 7 and the constancy of the derived values for $k_i k_p$ are the strongest arguments supporting the proposed kinetic scheme for this most unusual polymerization.

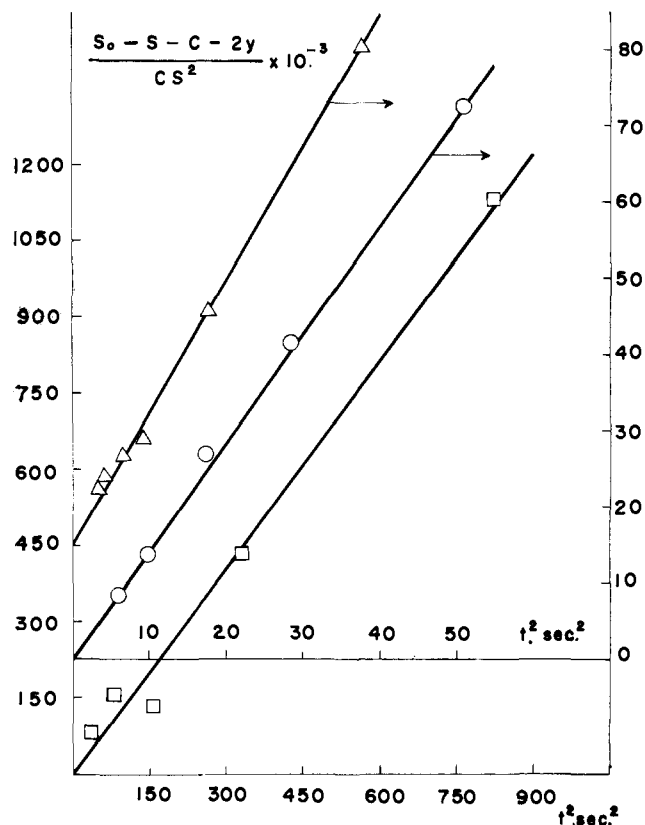To determine k_i, it was necessary to assume the value for k_p. Although this procedure is justified,

Fig. 7.—Kinetics in the stirred-flow reactor. Plot of $(S_0 - S - C - 2y)/CS^2$ vs. t^2. The upper two lines refer to the upper time^2 scale and the right-hand $(S_0 - S - C - 2y)/CS^2$ scale. The highest line is shifted up by 15 units, and the respective co-ordinate is multiplied by a factor of 10. □, run 21, $[\sim N^-]_0 = 3.1 \times 10^{-3} M$, $[S]_0 = 29 \times 10^{-3} M$, $k_i k_p = 1340$; O, run 23, $[\sim N^-]_0 = 2.9 \times 10^{-3} M$, $[S]_0 = 345 \times 10^{-3} M$, $k_i k_p = 1530$; △, run 22, $[\sim N^-]_0 = 3.1 \times 10^{-3} M$, $[S]_0 = 99 \times 10^{-3} M$, $k_i k_p = 1790$.

since k_p was independently determined by studying the kinetics of homopropagation of living polystyrene,[1] it would be more elegant to avoid this assumption and to use only the data derived from studies of the system living polyvinylnaphthalene–styrene. On mixing a relatively large excess of styrene with living polyvinylnaphthalene, we may assume that the complex is formed instantly and the reaction involves two steps only— a slow initiation

$$\text{complex} + \text{styrene} \longrightarrow \sim S^- \quad k_i$$
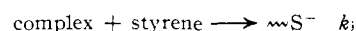
and a rapid propagation

$$\sim S^- + S \longrightarrow \sim SS^- \quad k_p$$
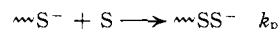
Such a system of consecutive reactions was discussed[11] and it was found that the ratio k_p/k_i is determined by $[M]_0/[I]_0$, the ratio of initial concentration of monomer to initiator and by the factor f which denotes the fraction of initiator used in the reaction. These entities are correlated by uhe relation[11]

$$[M]_0/[I]_0 = (k_p/k_i)\{\ln (1 - f)^{-1} - f\} + f$$

In our system we may assume the initial concentration of living vinylnaphthalene ends to be $[I]_0$, and using stop-flow technique to determine the final concentration of $\sim S^-$ ends from the asymptotic value of the optical density at 340 mμ observed after the living ends were mixed with the required excess of styrene $([M]_0 = [S]_0)$. The extinction coefficient of the complex at 340 mμ is determined from the initial and final optical

(11) M. Szwarc, *Makromol. Chem.*, **35**, 132 (1960).

TABLE VII

KINETICS OF STYRENE ADDITION TO LIVING VINYLNAPHTHALENE IN A STIRRED-FLOW REACTOR

$T = 25°$; solvent, THF; counter-ion, Na$^+$

Run	x_0, moles/l. × 10³	S_0, moles/l. × 10³	t, sec.	S, moles/l. × 10⁴	C, moles/l. × 10⁴	y, moles/l. × 10³
18	2.62	4.62	29.4	1.18	1.25	0.08
18	2.69	4.53	20.3	1.57	1.23	.08
18	2.66	4.55	21.1	1.62	1.25	.09
18	2.70	4.46	10.3	2.47	1.11	.06
18	2.71	4.40	7.75	2.81	1.02	.04
18	2.70	4.38	6.25	2.97	0.92	.03

$$k_i k_p = 1260 \ \{l./\text{mole sec.}\}^2$$

Run						
19	2.54	11.94	26.8	2.66	1.53	0.18
19	2.61	11.65	19.0	3.22	1.52	.17
19	2.63	11.51	12.0	4.39	1.46	.15
19	2.66	11.33	9.62	5.28	1.46	.15
19	2.63	11.41	7.96	5.49	1.37	.12
19	2.61	11.43	6.52	6.88	1.37	.12

$$k_i k_p = 1160 \ \{l./\text{mole sec.}\}^2$$

Run						
21	3.03	29.67	28.6	3.34	1.89	0.36
21	3.09	29.17	18.3	5.09	1.92	.35
21	3.11	29.03	12.7	8.36	1.95	.41
21	3.08	29.25	9.16	8.14	1.85	.27
21	3.22	28.08	6.67	10.27	1.90	.26

$$k_i k_p = 1340 \ \{l./\text{mole sec.}\}^2$$

Run						
20	3.46	54.36	18.7	6.98	2.18	0.57
20	3.43	54.87	13.9	9.19	2.17	.55
20	3.53	53.50	11.0	11.75	2.23	.57
20	3.58	52.78	8.43	15.68	2.26	.59
20	3.53	53.42	6.40	17.81	2.22	.51

$$k_i k_p = 1160 \ \{l./\text{mole sec.}\}^2$$

Run						
22	3.07	100.46	19.46	8.25	1.92	0.62
22	3.09	99.79	13.37	11.73	1.94	.60
22	3.11	99.41	9.73	16.85	1.94	.64
22	3.13	98.77	8.07	18.08	1.97	.57
22	3.18	97.35	6.33	20.02	2.00	.51
22	3.17	97.60	6.06	22.13	2.00	.54

$$k_i k_p = 1790 \ \{l./\text{mole sec.}\}^2$$

Run						
23	2.89	347.7	7.15	49.4	1.55	1.10
23	2.89	348.3	5.37	63.3	1.57	1.07
23	2.98	340.4	4.18	74.0	1.66	1.03
23	2.89	348.1	3.17	101.1	1.59	1.02
23	2.98	340.6	2.46	121.4	1.68	1.00

$$k_i k_p = 1530 \ \{l./\text{mole sec.}\}^2$$

TABLE VIII

KINETICS OF STYRENE ADDITION TO LIVING VINYLNAPHTHALENE IN A STIRRED-FLOW REACTOR

Solvent, THF; $T = 25°$; counter-ion, Na$^+$

Run	$[\sim N^-]_0$ × 10³ moles/l.	$[S]_0$ × 10³ moles/l.	$[S]_0/[\sim N^-]_0$	$k_i k_p{}^a$ (l./mole sec.)²
18	2.7	4.5	1.65	1260
19	2.6	11.5	4.4	1160
21	3.1	29	9.4	1340
20	3.5	54	15.4	1160
22	3.1	99	32	1790(?)
23^b	2.9	345	119	1530(?)

Av. $k_i k_p$ 1230

^{a} The results marked (?) are rejected in calculation of the average $k_i k_p$. ^{b} The temperature increased due to the rapid reaction.

densities at 440 and 340 mμ. Thus derived f-values, in conjunction with [liv. ends]$_0$ and [S]$_0$ are listed in Table IX and were used to calculate k_p/k_i. The results are given in the fifth column of Table IX; and since $k_p k_i$ was determined previously (see Table VIII), the

values k_i and k_p could now be calculated. These are listed in the last two columns of Table IX and show that our estimate of $k_p = 600$ l./mole sec. was correct and the proposed set of rate constants is self-consistent.

TABLE IX

DETERMINATION OF k_p/k_i FROM FRACTION OF COMPLEX CONVERTED INTO $\sim$S$^-$

$[S]_0$ × 10³ moles/l.	[Liv. ends] × 10³ moles/l.	$[S]_0/$[liv. ends]	f	k_p/k_i	k_p, l./mole sec.	k_i, l./mole sec.
90.9	4.79	18.0	0.275	378	682	1.80
104.4	4.53	22.0	.308	362	668	1.84
108.2	3.98	26.2	.371	281	588	2.09
111.0	3.94	27.2	.338	362	667	1.85
121.0	4.21	27.7	.362	315	623	1.97
169.2	3.73	44.4	.462	278	585	2.11
234.1	3.90	59.1	.520	304	611	2.01
244.0	3.84	62.6	.538	265	571	2.15
258.5	3.73	68.4	.537	291	598	2.06
279.0	3.59	76.5	.551	304	612	2.01
280.3	3.59	77.2	.525	350	656	1.88
305.5	3.41	88.6	.580	307	615	2.00
295.6	3.05	95.8	.578	334	641	1.92
323.1	3.29	97.2	.594	315	622	1.98
338.0	3.19	104.8	.596	337	644	1.91
341.4	3.17	106.9	.587	358	663	1.86
348.2	3.13	110.4	.593	358	663	1.86

Av. 323 ± 29 629 ± 28 1.96 ± 0.09

Discussion of Styrene Addition to Living Polyvinylnaphthalene.—The formation of the intramolecular complex (λ_{max} 440 mμ) on addition of styrene to a solution of living polyvinylnaphthalene is the most striking and intriguing feature of this reaction.

Complexes of aromatic hydrocarbons with living polymers were reported by Levy and Cohen-Bosidan.[12] Medvedev, et al.,[13] and by Khanna, Levy, and Szwarc.[14] Medvedev's group observed the appearance of a new band at 445 mμ and disappearance of the styryl$^-$ band (λ_{max} 340 mμ) on addition of anthracene to living polystyrene. They observed also that the resulting solution polymerizes added styrene, although at a very low rate, and they noticed that the 340-mμ band did not appear and the 445-mμ band persisted, even when a large excess of styrene polymerized. The importance of this observation escaped them, and they emphasized the more trivial copolymerization aspect of the system anthracene–styrene.

Khanna, Levy, and Szwarc[14] independently made the same observations and were impressed by the persistence of the 440-mμ band in experiments containing an equivalent amount of anthracene in respect to living polystyrene. Although a substantial amount of added styrene polymerized, the 340-mμ band did not reappear. Two explanations were offered to account for this behavior: (1) The polymerization of styrene was due to a process in which the monomer is squeezed between the last styrene segment and the terminal anthracene unit. (2) The system is in equilibrium, i.e.

$$\sim S^-, A \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} \sim S^- + A,$$
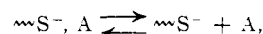
and while the anthracenated "dormant" polymers do not grow, the dissociated units polymerize. Of course, if the rates of dissociation and association are large in comparison with the rate of polymerization, all the polymers—dormant or active—get their share of monomer. To distinguish between these two alternatives, Khanna, Levy, and Szwarc[14] determined the initial rate of polymerization as a function of excess free an

(12) M. Levy and F. Cohen-Bosidan, *Polymer*, **1**, 517 (1960).

(13) A. A. Arest-Yakubovich, A. R. Gantmakher, and S. S. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, **139**, 1351 (1961).

(14) S. N. Khanna, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 747 (1962).

thracene. Explanation 1 predicts no change in the rate, while explanation 2 demands a reciprocal relation of the initial rate with excess free anthracene. The results proved the correctness of the equilibrium suggestion and permitted the determination of the equilibrium constant of the association at $\sim 10^6$ l./mole. The subsequent work of Asami, Khanna, Levy, and Szwarc[15] proved that the dissociation and association are fast. and thus the molecular weight of the resulting polymers are similar in the presence or absence of anthracene.[13,14]

The findings of Medvedev's group[13] and of our group[14] show how cautious one should be in drawing conclusions based on such observations as the one reported by Tobolsky, Rembaum, and Eisenberg[16] or by Tobolsky and Hartley.[17] These workers tried to distinguish between the initiators acting as electron donors[18] and those forming bonds with the monomer[19] by analyzing the polymer for the initiator fragments. Medvedev remarked[13]: "..... observation of initiator fragments in polymers cannot serve as proof of bond formation in the initiation step, since aromatic components could enter the chain during its growth." We could add that they may also appear on the *end* of a polymer as a result of the complexing process.

Although anthracene, pyrene, chrysene, etc., form complexes with living polystyrene, naphthalene does not form such a complex or forms it only to a negligible extent. Neither Medvedev's group[13] nor ours (unpublished results from our laboratory) observed any change in the propagation rate constant of living polystyrene on addition of a large excess of naphthalene. Medvedev's group reports, however, a change in the spectrum, namely a shift of the maximum from 340 to 550 mµ. We did not notice such a shift and suspect that the "shift" reported by Medvedev arises from a "transformation" of living polystyrene. reported by Spach, *et al.*,[20] which is accelerated by naphthalene.

The formation of a complex involves a loss of translational entropy of the aromatic hydrocarbon. However, complexing of a naphthyl moiety with a styryl⁻ ion placed on the adjacent segment requires a lesser decrease of the entropy of the system than the analogous process involving free naphthalene. Thus, although the latter process is unfavorable, the former does take place.

The complex formation is a reversible process. For example, the equilibrium constant for the process

(15) R. Asami, S. Khanna. M. Levy. and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1821 (1962).

(16) A. V. Tobolsky, A. Rembaum, and A. Eisenberg. *J. Polymer Sci.*, **45**, 347 (1960).
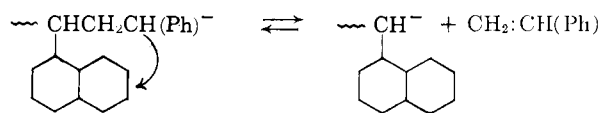
(17) A. V. Tobolsky and D. B. Hartley, *J. Am. Chem. Soc.*, **84**, 1391 (1962).

(18) (a) M. Szwarc, M. Levy, and R. Milkovich. *ibid.*, **78**, 2656 (1956); (b) M. Szwarc, *Nature*, **178**, 1168 (1956).

(19) D. H. Richards and M. Szwarc, *Trans. Faraday Soc.*, **55**, 1644 (1959).

(20) G. Spach. M. Levy, and M. Szwarc, *J. Chem. Soc.*, 355 (1962).

$\sim\!\!S^- + A \rightleftarrows \sim\!\!S^-,A$ was determined[14] to be $\sim 10^6$ l./mole. The experiments reported in Table IV imply the dissociation of the complex

and the rate constant of this process appears to be $\sim 10^{-4}$ to 10^{-5} sec.$^{-1}$ (judging from the time required for the reappearance of one half of the initial intensity of the absorption peak at 558 mµ). Since the bimolecular rate constant of the complex formation was determined to be 30 l./mole sec., the equilibrium constant of the association should be 10^3-10^4 l./mole. This value seems to be reasonable.

The slow addition of the second styrene molecule to the complex may be intrinsically a slow process or it may involve a "normal" addition to an "active" S⁻ unit, *i.e.*
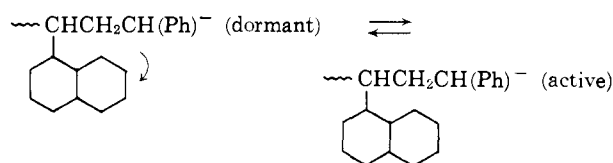
Were the second interpretation correct, the fraction of the "active" units would correspond to $\sim\!0.3\%$ of the complexed (dormant) one.

The nature of the complexes formed by aromatic hydrocarbons with living polymers is not definitely established. At present we are inclined to believe that the interaction results from charge-transfer forces; however, this is by no means certain and the formation of a covalent C–C bond must not be excluded.

Our observations show how intricate the relation may be in anionic copolymerization and how careful one should be in attributing a simple meaning to the reactivity ratios determined from a composition of the copolymer produced by anionic polymerization.

Note Added in Response to Dr. Tobolsky's Question.—Dr. Tobolsky observed a spectrum of stilbene in a polymer of α-methylstyrene initiated by diphenylacetylene (ref. 16) and inquires whether this is a sufficient proof for the initiation by bond formation. We did not investigate this particular case, and therefore we do not know the nature of this initiation. However, the appearance of the spectrum of stilbene in the polymer is not a sufficient proof for such an initiation. The same result may be obtained by complexing diphenylacetylene with the growing end.