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The Kinetics of Polymerization of Pentafluorostyrene.

Tzu-lee Huang

Louisiana State University and Agricultural & Mechanical College

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THE KINETICS OF POLYMERIZATION OF PENTAFLUOROSTYRENE

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Chemistry

by

**Tzu-Lee Huang
B.S., Prov. Chung-Hsing University, 1960
May, 1970**

To Shiao Lung-Lung

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ABSTRACT

Thermal polymerization of pentafluorostyrene (PFS) was carried out in bulk and in the presence of solvents. Comparison of molecular weights determined osmotically with those obtained using tritium-labeled AIBN indicates that termination occurs exclusively by combination. Molecular weights may be calculated from intrinsic viscosities using the equation $\bar{M}_n = 8.50 \times 10^5 [\eta]^{1.36}$. The solubility of poly-PFS was studied in a number of solvents. Values of $2k_d f / \delta^2$ were obtained for AIBN-initiated polymerization in bulk and in several solvents. From these values and molecular weight data, values of f and δ^2 were calculated, where $\delta^2 = 2k_t / k_p^2$. Both f and δ^2 show some solvent dependence. The thermal polymerization of PFS has a rate which is similar to that of styrene, and has an activation energy of thermal initiation which is much lower than that of styrene. These observations are difficult to explain in terms of the most accepted mechanism for styrene's thermal polymerization; that is, one which involves an atom-transfer reaction between a Diels-Alder dimer and another molecule of styrene. If this mechanism were to apply to PFS, a fluorine atom would have to be transferred. The transfer constant to PFS is zero; this fact also is relevant to the speculation on the mechanism of thermal initiation. Transfer to THF, fluorobenzene, methyl isobutyl ketone, methyl isopropyl ketone, benzonitrile, benzotrifluoride, hexafluorobenzene and some non-solvents were studied with or without a third solvent. Photopolymerization of PFS both in

bulk and in solvents were studied and the radical lifetime was measured by the rotating sector method. Both thermal and AIBN-initiated copolymerization of PFS-styrene and PFS-methyl methacrylate (MMA) were studied. For PFS-styrene, the values of r_2 , e_2 and Q_2 for PFS are 0.22, 0.74 and 0.69; for PFS-MMA, the values of these parameters are 0.91, 0.75 and 0.87. From the data obtained from chain transfer, absolute rate constant and copolymerization experiments, it is concluded that poly-PFS radical is more reactive than polystyryl radical but that the monomer is less reactive. The kinetics of copolymerization were studied also: for PFS-styrene, ϕ is 7.2 and for MMA it is 5.3. The kinetics of heteropolymerization of PFS were examined in the presence of methanol. It was shown that typical occlusion phenomena are operative in this system.

INTRODUCTION

Synthesis. The monomer 2,3,4,5,6-pentafluorostyrene (PFS) was synthesized for the first time in 1959 by Wall¹ in the United States and by Nield et al.,² in England. Pentafluorobromobenzene is obtained as one of the products from the synthesis of hexafluorobenzene by the pyrolysis of tribromofluoromethane.¹ It is then reacted as shown below:

An alternate route to pentafluorobromobenzene utilizes bromination of pentafluorobenzene in 65% oleum.³ Recently, Wall⁴ reported a third method of preparation of PFS: With vinyl lithium, prepared from 0.1 mole of PhLi and 0.025 mole of tetravinyltin, 0.1 mole of hexafluorobenzene gave 20% PFS. Pure PFS is a colorless liquid having b.p. 141-142° (760 mm)^{1,2} and n_D^{20} 1.4410-1.4420. Commercial PFS usually contains 0.5% t-butylcatechol as inhibitor.

This monomer is interesting because its structure is similar to styrene and yet it has 5 fluorine atoms on the ring. Furthermore, PFS polymer might be expected to have greater stability than polystyrene in the same way that Teflon is more stable than polyethylene. Indeed, Wall^{5,6} reported that PFS polymer (poly-PFS) has greater thermal stability and better radiation-resistance than polystyrene. The purpose of this study is to investigate the kinetics of polymerization of this interesting monomer.

Kinetics of Polymerization. The kinetic symbolism used in this study is in conformity with American conventions in polymerization kinetics.⁷ (See Appendix I.) There are four basic equations involved in a radical induced polymerization:

where I is initiator, $R^\bullet$ the primary radical, M the monomer, $M^\bullet$ a polymer radical regardless of chain length, and P a polymer molecule. Note that in Equation 4, a factor of 2 is introduced for the rate of disappearance of radicals. (See Appendix I.) When solvent is present in a polymerization system, two more steps may be added:

where $S^\bullet$ is the solvent radical, and S the solvent molecule. In order to derive useful kinetic expressions, it is assumed that (a) all rate constants are independent of chain length, so that $M_n^\bullet = M_{n+1}^\bullet = M^\bullet$ as implied in Equation 3; (b) the rates of formation and destruction of free radicals are equal (the steady state assumption); (c) the solvent radical formed in Equation 5 immediately initiates a new chain by Equation 6, i.e., there is no degradative chain transfer.⁸ If the

polymer chain length is very large, the monomer disappearance is predominantly due to the propagation reaction, and the overall rate of polymerization can be replaced by the rate of propagation.

$$-d[M]/dt = R_p = k_p [M^\bullet][M] \quad (7)$$

By the steady state assumption, the rate of initiation of radicals is equal to the rate of their destruction:

$$R_i = R_t \quad (8)$$

or

$$2k_d f[I] = 2k_t [M^\bullet]^2 \quad (9)$$

Combining Equations 7 and 9,

$$R_p = [M] \frac{R_i^{0.5}}{\delta} = \frac{(2k_d f)^{0.5}}{\delta} [M][I]^{0.5} \quad (10)$$

where $\delta = (2k_t)^{0.5}/k_p$.

The degree of polymerization, defined as the number of monomer units in the average polymer molecule, can be formalized as follows:

$$\bar{P} = \frac{-d[M]/dt}{d[P]/dt} \quad (11)$$

where $d[P]/dt$ represents the rate of production of polymer, and $-d[M]/dt$ the rate of consumption of monomer. If the growing radicals are terminated by mutual combination, as well as by transfer, then

$$\frac{d[P]}{dt} = k_t [M^\bullet]^2 + k_{tr,M} [M^\bullet][M] + k_{tr,S} [M^\bullet][S] + k_{tr,I} [M^\bullet][I] + \dots \quad (12)$$

By rearrangement of Equation 11 and combining with Equations 7-10, 12, we obtain

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_p + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + \dots \quad (13)$$

where $C_M = \frac{k_{tr,M}}{k_p}$, $C_S = \frac{k_{tr,S}}{k_p}$, and $C_I = \frac{k_{tr,I}}{k_p}$ are called the transfer constants to monomer, solvent and initiator, respectively. If R_p is taken to be constant and in the absence of initiator, Equation 13 becomes the Mayo equation for transfer to solvent⁹

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + C_S \frac{[S]}{[M]} \quad (14)$$

where $1/\bar{P}_0$ is the inverse of the degree of polymerization for bulk monomer (no solvent case), and the $1/\bar{P}_0$ value is dependent on the monomer and the temperature of the polymerization but it is independent of solvent. One way of measuring C_S is to use thermal initiation and Equation 14. A graph of $1/\bar{P}$ against $[S]/[M]$ should give a straight line with slope C_S . In another method, an initiator is used and the C_S value may be calculated from Equation 13. Value of $k_d f$ and δ^2 can be determined by plotting R_p against $[M][I]^{0.5}$, and $1/\bar{P}$ against R_p , as seen from Equations 10 and 13, respectively. The mechanism of radical termination, combination or disproportionation must be known before calculating transfer constants, R_i values. Equations 12 and 13 are true only when growing chains are terminated by mutual combination. If polymer radicals are terminated by disproportionation, Equations 12

and 13 should be replaced by

$$\frac{d[P]}{dt} = 2k_t[M\cdot]^2 + k_{tr,M}[M\cdot][M] + k_{tr,S}[M\cdot][S] + k_{tr,I}[M\cdot][I] + \dots \quad (15)$$

and

$$\frac{1}{P} = \frac{\delta^2}{[M]^2} R_P + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + \dots \quad (16)$$

Mechanism of Thermal Initiation. It has been observed that rigorously purified styrene and some other olefins gave reproducible polymerization rates in the dark and in the absence of initiators.^{119,120} This indicates that impurities which might act as initiators are not responsible for the thermal initiation. Flory¹²⁰ reported that the overall thermal polymerization is second order in styrene, and he suggested a bimolecular initiation mechanism involving a diradical intermediate:

However, some evidence^{12d} against the formation of diradical in the initiation step has since been reported. Mayo,²⁸ from studies of the amounts of low- and high-molecular-weight polymers formed in the styrene-bromobenzene system, concluded that the overall rate is actually 2.5 order in styrene. To explain this, Mayo^{109,110} suggested a termolecular initiation mechanism which involves a Diels-Alder type dimer as an intermediate and the reaction of this adduct with a third

styrene molecule in a molecule-induced homolysis step:

Mayo's mechanism is substantiated by the isolation of 1-phenyl-tetraline (and other derivatives) from heated styrene,^{51,61} by kinetic analysis,¹¹⁸ and by kinetic isotope effect studies.^{121,122,127,128} Pure styrene decolorizes diphenylpicrylhydrazyl (DPPH), and this would seem to indicate that radicals are formed. However, the DPPH¹ disappears faster than radicals are calculated to be produced based on the rate of appearance of thermal polymer.⁶⁹ This can be explained⁶² by postulating that the DPPH reacts with the dimer to oxidize it:

The activation energy for this reaction is found to be 23 kcal/mole

close to that of thermal polymerization of pure styrene (21.0 kcal/mole²⁸). However, Lasswell¹²⁶ found that the DPPH disappears rapidly in vinyl-mesitylene, stilbene, cyclohexane and all other solvents except benzene. Thus the reaction of DPPH appears to be much more complicated than what one would expect; the DPPH may react with the monomer and the solvent as well as the dimer. Oxygen⁶² also spontaneously reacts with styrene with an activation energy of 24 kcal/mole. Apparently oxygen also undergoes a molecule-induced homolysis reaction with the adduct.

This mechanism for spontaneous autoxidation of styrene is substantiated by the identification of 4-phenyl-tetralone in styrene which reacted with oxygen in the presence of inhibitors to prevent extensive autoxidation:¹²³

Mayo's mechanism may be valid for styrene as well as other vinyl monomers such as 2-vinylfuran,⁵⁹ 2-vinylthiophene.⁵⁸ However, a recent study by Brown¹¹⁷ indicates that a more extended reaction scheme for the thermal polymerization of styrene involving both the Diels-Alder dimer and the diradical intermediate may be needed. More

discussion will be given later in the section on the thermal initiation mechanism of PFS (see p. 54).

The Rotating Sector Method. In the case of photopolymerization, primary free radicals are produced from the decomposition of initiator excited by the absorption of light (usually in the ultraviolet region). The rate of production of these radicals is proportional to the intensity of the absorbed light, $I_{\text{abs.}}$.

$$R_i = 2f \cdot I_{\text{abs.}} \quad (17)$$

where $I_{\text{abs.}}$ is the quanta absorbed in moles/liter/sec, and f the efficiency of chain initiation. (Usually f is less than 1 due to cage reactions). Beer's law states that:

$$I_{\text{abs.}} = I_0(1 - e^{-\epsilon[S] \cdot \ell}) \approx I_0 \cdot \epsilon \cdot [S] \cdot \ell$$

where I_0 is the intensity of incident light, ϵ the extinction coefficient of the initiator, $[S]$ the sensitizer concentration, and ℓ the optical path length. Eq.17 then gives:

$$R_i = 2f \cdot I_0 \cdot \epsilon \cdot \ell \cdot [S] \quad (18)$$

When steady state conditions are reached,

$$\frac{d[M\cdot]}{dt} = 0 = 2f \cdot I_0 \cdot \epsilon \cdot \ell \cdot [S] - 2k_t[M\cdot]^2 \quad (19)$$

and Equation 19 may be substituted into Equation 7, yielding

$$R_P = k_p[M] \left\{ \frac{2f \cdot I_0 \cdot \epsilon \cdot \ell \cdot [S]}{2k_t} \right\}^{0.5} \quad (20)$$

Thus, the rate of polymerization is proportional to the square root of light intensity and photosensitizer concentration.

Equations 19 and 20 are valid when the steady state of radical concentration is reached, but they are not valid at the start of the irradiation. The study of this non-steady state condition is the basis of the rotating sector technique, which at present appears to be the most accurate and dependable method of determining the rate constants in polymerization processes.¹⁰ A concept of the average lifetime of a growing polymer chain, τ_s , is introduced in the rotating sector method. This quantity is defined as the ratio of radical concentration at the steady state to the rate of disappearance of radicals

$$\tau_s = \frac{[M^\bullet]_s}{2k_t [M^\bullet]_s^2} = \frac{1}{2k_t [M^\bullet]_s} \quad (21)$$

Recalling Equation 7, a relationship between k_p and k_t is obtained:

$$\tau_s = \frac{k_p [M]}{2k_t R_{Ps}} \quad (22)$$

Equations 10 and 22 contain only two variables, and therefore individual values of k_p and k_t may be obtained. The theory of non-steady state kinetics and the evaluation of radical lifetime, τ_s , by intermittent illumination, is discussed by Melville and Burnett¹⁰ in detail. Only the results will be mentioned here. A sector is driven by a synchronous motor through a set of gears so as to give

varying rotation speeds. (See Appendix II). The light can be flickered at chosen intervals depending on the sector speed and the dark to light ratio, r , of the sector. This causes the radical production to be started and stopped at the chosen interval. For example, consider a sector with $r = 1$ (i.e., dark and light area equal). When the sector rotates very slowly, the radical concentration will be able to reach the steady state level during the light period and drop completely to zero during the dark period. In this extreme case, the rate of photo-polymerization will be

$$R_{P_{avg}} = \frac{1}{r+1} R_{Ps} = 0.5R_{Ps}$$

where R_{Ps} denotes the rate of polymerization under steady light. This is the so-called "lower limit" for the polymerization rate. If, on the other hand, the sector rotates very fast, the effect is the same as steady light, but the light intensity will be reduced by a factor of $r+1 = 2$. Since the rate of polymerization is proportional to the square root of the light intensity, the rate in this case will be

$$R_{P_{avg}} = \left(\frac{1}{1+r}\right)^{0.5} R_{Ps} = 0.708R_{Ps}$$

This is called the "upper limit" for the photopolymerization rate. Now, if we choose a sector speed between these two extreme limits, the rate will lie between the upper and lower limits, i.e.,

$\frac{1}{r+1} R_{Ps} < R_{P_{avg}} < \left(\frac{1}{1+r}\right)^{0.5} R_{Ps}$ or $0.5R_{Ps} < R_{P_{avg}} < 0.708R_{Ps}$. In this case, the radical concentration will not reach the steady state value but will lie between the two extreme values of $[M\cdot]$. An

experimental curve is obtained by measuring the polymerization rates at different sector speeds, R_p , comparing with those obtained at steady light, R_{ps} , and plotting the ratio R_p/R_{ps} against $\log \lambda$, where λ is the flash time measured by stop watch. Theoretical curves for different r values can be constructed (by plotting R_p/R_{ps} vs. $\log m$) using the following equations:¹⁰

$$\frac{R_p}{R_{ps}} = \frac{1}{r+1} \left\{ 1 + \frac{1}{m} \ln \left[\frac{rm}{1+R_{ps}/R_{p2}} + 1 \right] \right\} \quad (23)$$

$$\frac{R_{p2}}{R_{ps}} = \frac{rm \tanh m + [r^2 m^2 \tanh^2 m + 4(rm + \tanh m) \tanh m]^{0.5}}{2(rm + \tanh m)} \quad (24)$$

$$\tau_s = \frac{\lambda}{m} \quad (25)$$

where m is the ratio of time of flash to the lifetime of kinetic chain. Substitution of Equation 24 in 23 will give the values of R_p/R_{ps} in terms of m and r only. Burnett and Melville¹⁰ tabulated the values of R_p/R_{ps} as function of m for various values of r . The τ_s value can be calculated from the difference between the theoretical and experimental curves as implied by Equation 25. Usually an average value is taken and is called the "average lifetime".

The above discussion is based on three important assumptions:

- (1) The thermal (dark) rate is negligible, (2) the transition from light to dark conditions is sharp, and (3) termination occurs by only one mechanism. If the thermal rate is not negligible, the two curves (experimental and theoretical) will not meet at the lower (slow sector

speed) region. In this case in constructing theoretical curve, it is necessary to allow for thermal rate as given by Equations 26-28:

$$\frac{R_P}{R_{Ps}} = \frac{1}{r+1} \left\{ 1 + zr + \frac{1}{m} \ln \left[\frac{1+R_{P1}/R_{Ps}}{1+R_{P2}/R_{Ps}} \right] \left[\frac{1+z^{-1}R_{P2}/R_{Ps}}{1+z^{-1}R_{P1}/R_{Ps}} \right] \right\} \quad (26)$$

$$\frac{R_{P2}}{R_{Ps}} = \frac{[R_{P1}/R_{Ps}] + \tanh m}{1 + [R_{P1}/R_{Ps}] \tanh m} \quad (27)$$

$$\frac{R_{P1}}{R_{Ps}} = \frac{-(1-z^2) \tanh zrm \tanh m + \{(1-z^2)^2 \tanh^2 zrm \tanh^2 m + 4(\tanh zrm + z \tanh m)(z \tanh m + z^2 \tanh zrm)\}^{\frac{1}{2}}}{2(\tanh zrm + z \tanh m)} \quad (28)$$

where z is the ratio of the thermal to overall photochemical rates.

R_{P1} and R_{P2} are proportional to radical concentrations at the beginning - and end of the light flash, respectively. The computation is complicated, and a computer program has been written by Mr. H. Streiffer (Department of Chemistry, Louisiana State University) and was used in this study. Table 17 lists some theoretical values of R_P/R_{Ps} computed by this program. These data allow for thermal corrections from $z = 0.01$ to 0.04 and they are not available in the literature. Dainton¹¹ showed that assumption (2) is usually valid except at very low sector speeds. Assumption (3) is usually satisfied for the polymerization of styrene. Most experimental evidence¹² has shown that the termination reaction between two polystyryl radicals is an exclusive combination process for temperatures up to 80°C . Experiments using a labeled

initiator were used to show that PFS also undergoes termination by combination; these data have been published¹³ and will be present in this thesis also. If first order radical termination as well as mutual termination (combination or/and disproportionation) occurs, two curves (experimental and theoretical) will not meet at the upper (high sector speed) region, and a special calculation¹⁰ will be required to account for this. However, if both the dark rate and more than one radical termination mechanism become important at the same time, they tend to compensate each other and normal curves are obtained.

Copolymerization. In the copolymerization of two types of monomers, four chain propagating reactions and three termination steps are involved:

where M_1 = monomer 1, M_2 = monomer 2, $M_1 \cdot$ is a polymer radical having monomer 1 at the chain end, $M_2 \cdot$ is a polymer radical having monomer

2 unit at the chain end, k_{12} is the rate constant for reaction of polymer radical having monomer 1 at the end of chain with monomer 2, and so on. Here again, some assumptions have to be made in order to obtain useful kinetic expressions: (1) velocity coefficients are independent of radical size, (2) the chain length is great and total rate of monomer consumption may be taken to be that in propagating reactions, and (3) a steady state in radical concentrations exists. Using these simplifications, one can easily show that

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (36)$$

where $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$. r_1, r_2 are called "monomer reactivity ratios". Equation 36 is called the "copolymerization equation", and it was first introduced by Alfrey and Goldfinger.¹⁴ Evaluation of monomer reactivity ratios can be made by different methods.⁷ In this study, the Fineman-Ross method¹⁵ is adopted. By using the definitions $f = d[M_1]/d[M_2]$ and $F = [M_1]/[M_2]$, Equation 36 can be transformed to

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2 \quad (37)$$

The F value is known from the monomer composition and f can be determined by the analyses of the copolymer formed. Thus, a plot of $\frac{F}{f}(f-1)$ against $\frac{F^2}{f}$ gives slope = r_1 and intercept = $-r_2$. Reactivity ratios are characteristic of each monomer pair, and they are independent of the type of initiation. The actual initiator used affects the rate

but not the composition of the copolymer formed. On the other hand, it is necessary to indicate the temperature at which the copolymerization is carried out because reactivity ratios are temperature dependent; i.e., the two rate constants comprising the reactivity ratios do not, in general, have the same activation energy. There is some evidence indicating that solvents have no detectable effect on reactivity ratios; Mayo¹⁶ found identical reactivity ratios for the styrene-MMA system in benzene and acetonitrile (solvents of low and high dielectric constant, respectively) and in methanol (a solvent from which the polymer precipitates).

The Q - e Scheme. In addition to their obvious use in predicting the composition of a resulting copolymer, the monomer reactivity ratios can be used in a quantitative discussion of monomer and radical reactivity. The best known and the most widely used reactivity correlation is known as the Alfrey-Price Q - e scheme.¹⁷ This scheme expresses each propagation rate constant in terms of four parameters representing the basic reactivities and polarities of the two species concerned. If the polarity of the monomer and of its corresponding radical are assumed to be the same, then the following equations can be derived:

$$\begin{aligned}k_{11} &= P_1 Q_1 \exp(-e_1^2) \\k_{12} &= P_1 Q_2 \exp(-e_1 e_2) \\k_{22} &= P_2 Q_2 \exp(-e_2^2) \\k_{21} &= P_2 Q_1 \exp(-e_1 e_2)\end{aligned}$$

where P and Q are proportional to the basic reactivities of the radical and monomer respectively, and e is proportional to the charge on the monomer unit. Thus, by recalling the definition of r_1 and r_2

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (38)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (39)$$

$$r_1 r_2 = \exp[-(e_1 - e_2)^2] \quad (40)$$

Upon rearrangement,

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{0.5} \quad (41)$$

$$Q_2 = \frac{Q_1}{r_1} \exp[-e_1(e_1 - e_2)] \quad (42)$$

Clearly, a standard reference monomer is needed in the assignment of Q, e values. Styrene has been chosen for this purpose, and the scheme has been found to be self-consistent when $Q_1 = 1.0$, $e_1 = -0.80$ for styrene. The factor Q is a measure of general reactivity of the monomer and its corresponding radical. Resonance stabilization affects both monomer and radical, but the effect on the radical is usually greater. Therefore, the greater the Q value, the greater will be the relative resonance stabilization of the radical produced from the monomer, and the higher will be the reactivity of the monomer. The greater the Q of a monomer, the less reactive will be its corresponding polymer radical. The factor e is a measure of polarity

of the monomer and the corresponding radical (assumed to be of equal polarity in the Q - e scheme). The more positive the e value, the more electropositive (electron-poor) will be the reaction site (usually at the vinyl double bond of a monomer); the more negative the e value, the more electron-rich will be the monomer.

The ϕ Factor. The ϕ factor, another important parameter in copolymerization, can be derived from the kinetic measurements.

While the composition of the copolymer is governed largely by four propagation rate constants in terms of r_1 and r_2 values, the rate of copolymerization depends on the rates of initiation, termination, and propagation. According to the steady state assumption, the rate of initiation is equal to the rate of termination, i.e.:

$$R_i = 2k_{t11}[M\cdot]^2 + 2k_{t12}[M_1\cdot][M_2\cdot] + 2k_{t22}[M_2\cdot]^2 \quad (43)$$

The over-all rate of copolymerization is given by

$$R_p = \frac{-d([M_1] + [M_2])}{dt} = k_{11}[M_1\cdot][M_1] + 2k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] \quad (44)$$

By combining Equations 43 and 44, it can be shown that

$$R_p = \frac{\{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2\}R_i^{0.5}}{\{r_1^2\delta_1^2[M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2\delta_2^2[M_2]^2\}^{0.5}} \quad (45)$$

$$\text{where } r_1 = \frac{k_{11}}{k_{12}}, \quad r_2 = \frac{k_{22}}{k_{21}}, \quad \delta_1^2 = \frac{2k_{t11}}{k_{11}^2}, \quad \delta_2^2 = \frac{2k_{t22}}{k_{22}^2} \text{ and } \phi = \frac{k_{t12}}{2(k_{t11}k_{t22})^{0.5}}.$$

The factor ϕ is a measure of the importance of cross-termination in copolymerization. Usually $\phi > 1$ means that radicals of different polarities terminate with each other (cross-termination) in preference to the termination of the same kind of radicals. The value of ϕ indicates that the cross-termination step in copolymerization pairs is quite important. It is a qualitative fact that ϕ is largest in those systems in which the propagation processes show a tendency towards alternation ($r_1 r_2$ small).

HOMOPOLYMERIZATION

I. EXPERIMENTAL SECTION

Purification of Monomer. PFS was purchased from the Imperial Smelting Corp. of England as a light yellow liquid containing 0.5% *t*-butylcatechol as inhibitor. Purification was accomplished by prepolymerization at 60° for 6 hr followed by distillation under nitrogen at 34° (25 mm). The cycle was repeated until a constant rate of thermal polymerization was reached. The correct thermal rate was found to be $5.70 \times 10^{-7} \text{ M sec}^{-1}$ at 60°C. The pure monomer has b.p. 141-142° (760 mm)^{1,2} and n_D^{20} 1.4410-1.4420, and it is colorless.

Isolation of the Polymer. Polymer was isolated by a modification of the freeze-dry technique developed by Lewis and Mayo for styrene¹⁹; the modifications were necessary since poly-PFS is insoluble in benzene, and the freezing point of the solvent tetrahydrofuran (-65°) precludes its use in freeze-drying. The contents of ampoules were washed into a 125 ml flask with 50-100 ml of THF, the solvent was evaporated under a moderate vacuum, 50 ml of benzene was added, the suspension was frozen in Dry Ice-acetone, and the benzene was allowed to sublime off under full vacuum. The cycle was repeated until constant weight was obtained.

In the runs where tritium-labeled azobisisobutyronitrile (AIBN) was used as initiator, the polymer was dissolved in 15 ml of

THF and precipitated from 250 ml of cold methanol (-30°), filtered immediately and washed with cold methanol. This cycle was repeated three times. A typical control was as follows: 1 ml of PFS was polymerized to 20.3% conversion using 4.57×10^{-4} M AIBN-t at 60° . The polymer isolated after three precipitations showed a weight loss of about 5%. A mixture of 4.6×10^{-5} mol of AIBN-t and 0.052 g of inactive poly-PFS was prepared in PFS monomer and purified in the same way; the isolated polymer had an apparent activity of about 10 dpm. Similar controls at lower AIBN-t molarities had proportionally less activity in the recovered polymer.

Molecular Weight Determinations. A Hewlett-Packard Model 501 membrane osometer was used to measure molecular weights. Conditions were 30° , S&S 0-8 membrane, and methyl isobutyl ketone (MIBK) as solvent. Molecular weights also were measured by counting polymer prepared with tritium-labeled AIBN as initiator and by assuming that each polymer molecule contains one entire AIBN molecule. The radioactive polymer was dissolved in 8 ml of counting solution prepared by diluting 20 ml of Packard concentrated scintillation solution to 500 ml with fluorobenzene as a solvent. Counting was done with a Packard Tri-Carb Model 3003 liquid scintillation spectrometer. Efficiencies were determined using the external standard of this instrument, calibrated against acetone-quenched standards. The AIBN-t used was prepared by Dr. T.R. Fiske using method of Thiele and Heuser,^{20,21} and had a specific activity of 3.047×10^9 dpm/mol.

Viscosity Measurements. Viscosities were measured at 30° using Cannon-Ubbelohde viscometers and concentrations of 0.05-0.07g/25 ml

of MIBK. Intrinsic viscosities were determined by extrapolation of specific viscosities to infinite dilution. Intrinsic viscosities could also be calculated using the following equation

$$[\eta] = \frac{[1 + 2.08\eta_{sp}]^{\frac{1}{2}} - 1}{0.75 C_v}$$

at 30° and in MIBK as solvent, where C_v is the polymer concentration in grams per 100 ml of solution at 30° and $\eta_{sp} = (t/t_0) - 1$, where t and t_0 are the flow times for solution and pure solvent, respectively.

Kinetics. Rates of thermal (uncatalyzed) and catalyzed polymerizations were followed by using either a 10 ml dilatometer or by an ampoule technique. The density of PFS was found to 1.414g/ml at 30°, 1.388g/ml at 46.2°, and 1.366g/ml at 60°. The plot of % polymer in monomer (i.e., % conversion) vs. density is linear to about 25% conversion, the highest calibration point. The data at 60° give the relation % conversion = (0.1040)(% contraction). This relation is similar to that for other substituted styrenes.²²⁻²⁴ The density measurements on polymer-monomer mixtures extrapolate to give 1.5921g/ml for the density of poly-PFS at 100% conversion. The density of polymer was measured by pressing it under 90,000 psi, placing it in a pycnometer which was then filled with mercury and heated to 120° for 3 hr, cooled, again filled with mercury and heated to 60°. The experimental value for the polymer density by this procedure is 1.5499g/ml. This density of solid polymer is about 2.6% less than that calculated for an infinitely concentrated solution of polymer in its own monomer. Similar behavior has been reported for

styrene.^{25,26}

Solubility. Poly-PFS is soluble in methyl ethyl ketone (MEK), MIBK, THF, ethyl acetate, ethyl propionate, fluorobenzene, benzotrifluoride, hexafluorobenzene; slowly soluble or slightly soluble in pyridine, acetone, methyl isopropyl ketone, methyl acetate, benzonitrile, chlorobenzene, and acetophenone; and insoluble in benzene, toluene, ethylbenzene, cumene, bromobenzene, iodobenzene, carbon tetrachloride, chloroform, carbon disulfide, methanol, ethanol, ether, tetralin, dioxane, decalin, cyclohexane, hexane, heptane, *o*-dichlorobenzene, benzyl alcohol, phenyl ether, methyl benzoate, ethyl benzoate, benzophenone, anisole, N,N-dimethylformamide (DMF), ethylene glycol, aniline, nitrobenzene, *p*-chloroanisole, bromocyclohexane and benzotrichloride.

Determination of Absolute Rate Constants. Radical lifetimes were measured by the rotating sector technique.¹⁰ The set-up was as follows: The reaction cell was irradiated by the light from a 100-watt General Electric Ultraviolet Mercury Quartz lamp with a U.V. transmitting filter (Corning C.S. 0-52) to give maximum transmittance at 366 mμ. The light was collimated by three lenses to produce a parallel beam through the reaction cell in a 30°C bath. Two 60° sectors (*r* = 2) were cut from a disc made from a blackened sheet of aluminum. This disc was driven by a Bodine synchronous motor through a set of gears which could be varied so as to give rotation speeds ranging from 60 to 0.06 r.p.m. The light intensity was practically constant throughout the experiment since a check of

the plot of the rate vs. the square root of the sensitizer concentration (Eq.20) always give an excellent linear relationship (See Appendix I). Azocyclohexanecarbonitrile (ACHN), purchased from Koch-Light Laboratories Ltd. of England, was recrystallized twice from methanol and melted at 114-115°. AIBN was purified by the same procedure and melted at 103-104°. In all runs, ACHN was used as a photosensitizer whereas AIBN was used as an initiator for all thermal (dark) runs. The reaction was followed with a 10 ml dilatometer, and the densities of poly-PFS-monomer solutions were determined at 30°C with a pycnometer. The data of 30° give the relation: % conversion = (0.0950) (% contraction).

The thermal rate of polymerization in the dark was measured in each run, and the treatment allowing for thermal rate¹⁰ was employed in the calculation of radical lifetime, τ . The rates of initiation were calculated from the rates measured dilatometrically, and values of $\delta^2 = 2k_t/k_p^2$ were obtained from runs with AIBN as initiator.

DPPH Scavenging Experiments. In experiments in which the disappearance of diphenylpicrylhydrazyl (DPPH) was followed by absorption measurements, the reaction vessels were cells which were optically matched at 520 mμ, and the change in absorption was followed at this wavelength with a Beckman DK Spectrophotometer. The DPPH concentrations used were 9.79×10^{-5} M. An electrically heated cell holder was used, and the temperature was regulated to within $\pm 1^\circ$ during the reaction times.

II. RESULTS AND DISCUSSION

Thermal Polymerization of PFS in Bulk at Different Temperatures.

The purified monomer gave reproducible rates of uninitiated polymerization in the dark at different temperatures. Table 1 gives the data. An Arrhenius plot of $\log R_p$ against $1/T$ shows a good linear relationship (Figure 1), and the thermal rate of PFS, therefore, can be expressed by the following equation:

$$R_{p,th}(\%/hr) = (2.37 \times 10^9) \exp(-16,800/RT)$$

For thermal polymerization of styrene, the equation is:²⁹

$$R_{p,th}(\%/hr) = (3.55 \times 10^{11}) \exp(-19,100/RT)$$

Figure 2 is a plot of $\log \bar{M}_n$ against $\log R_p$ using the data from Table 1. It can be seen that there is a good reciprocal relation existing between rate and molecular weight for PFS thermal polymerization. This is, of course, an evidence for the validity of Equation 13 in this particular polymerization. This observation is true for styrene also.^{29c} An Equation relating $\bar{P}$ to temperature may be derived from Equation 11:^{30,57e}

$$\bar{P} = \frac{-d[M]/dT}{d[P]/dT} = \frac{k_p[M\cdot][M]}{k_t[M\cdot]^2 + k_{tr,M}[M\cdot][M]}$$

In the absence of initiator, by assuming chain transfer reactions are negligible, and by introducing $k = Ae^{-E/RT}$ and $[M\cdot] = \left[\frac{R_i}{2k_t}\right]^{1/2}$ where

$R_i = k_i(M)^a$ with a a constant, it is shown that

$$\frac{d \ln \bar{P}_n}{dT} = (E_p - E_t/2 - E_{i,th}/2)/RT^2 \quad (46)$$

If, on the other hand, transfer reactions are controlling the molecular weight, the following equation is obtained:^{57e}

$$\frac{d \ln \bar{P}_n}{dT} = (E_p - E_{tr,M})/RT^2 \quad (47)$$

where $E_{tr,M}$ is the activation energy for chain transfer to monomer; E_t , termination; E_p , propagation; and $E_{i,th}$ thermal initiation. In the thermal polymerization of PFS, as can be seen from Figure 3, a plot of $\log \bar{P}$ vs $1/T$ does give a good linear relationship which is expected from both Equations 46 and 47.

Molecular Weight Determinations. The polymerization of PFS was carried out under a number of experimental conditions (thermal and catalyzed) as shown in Tables 1 to 3. The molecular weight of the isolated polymers was determined by osmometry and by counting polymer prepared in the presence of tritium-labeled AIBN (AIBN-³H) assuming that termination is entirely by combination (*i.e.*, one mole of initiator is incorporated into each mole of polymer). Figure 4 shows the relationship between the number-average molecular weight, $\bar{M}_n$, and the intrinsic viscosity. The agreement between two methods (see Figure 4) shows that termination is entirely by combination within the accuracy of the molecular weight measurements. The line shown in

Table 1

Thermal Polymerization of PFS in Bulk at Different Temperatures

$^{\circ}\text{C}$	Hours	% Conv.	$R_{p,th} \times 10^2{}^a$	$[\eta]^b$	$\bar{P} \times 10^{-4}{}^c$	$\bar{M}_n \times 10^{-6}{}^d$	$1/T \times 10^3$	$[M]^e$	$R_p \times 10^6{}^f$
129	8.5	16.9	199	3.02	1.97	3.82	2.49	6.47	35.8
129	8.5	15.5	182	3.15	2.09	4.06	2.49	6.47	32.7
119	5	4.55	91.2	----	----	----	2.55	6.55	16.6
100	24	9.71	40.4	4.82	3.69	7.16	2.68	6.70	7.52
100	17.4	8.83	50.7	3.78	2.68	5.18	2.68	6.70	9.44
100	19.5	5.68	29.1	4.25	3.13	6.08	2.68	6.70	5.42
80	100.8	6.88	6.82	6.58	5.68	11.02	2.83	6.87	1.30
80	48	2.98	6.21	5.79	4.76	9.24	2.83	6.87	1.19
60	160	4.82	3.01	5.94	4.95	9.84	3.00	7.04	0.589
60	160	4.50	2.81	7.23	6.45	12.52	3.00	7.04	0.570

^aThermal rates in % per hour.

^bIntrinsic viscosities measured in MIBK at 30°.

^cCalculated by using Equation 48.

^d $\bar{M}_n = (194.1)\bar{P}$.

^eMonomer concentration calculated from density measurements, in mole/l.

^fThermal rates in M sec^{-1} .

Figure 1. Arrhenius Plot for Thermal Polymerization of PFS in Bulk.

Figure 2. Plot of $\log \bar{M}_n$ vs. $\log R_{P,th}$ for Thermal Polymerization of PFS in Bulk.

Figure 3. Plot of $\log \bar{P}$ vs. $1/T$ for Thermal Polymerization of PFS in Bulk. Dotted line shows the corresponding plot for styrene and with $\bar{P}$ calculated from Table 3-1 of Ref.12a.

Table 2
The Polymerization of PFS Initiated by AIBN-³H at 60°C

[AIBN- ³ H] × 10 ²	Time, hr (at 60°)	Convsn. %	Dpm in Polymer corrected ^a	Moles M × 10 ^{4b}	Moles I × 10 ^{7c}	$\bar{M}_n \times 10^5d$	[η] ^e
4.57	1.5	15.1	970	2.65	3.16	1.63	0.31
2.74	3.6	26.2	909	2.99	2.96	1.96	0.37
1.83	4	19.9	567	2.57	1.86	2.68	0.39
1.37	5	25.7	567	2.60	1.85	2.74	0.45
0.915	5.5	21.3	472	2.78	1.55	3.47	0.47
0.457	9	27.7	385	3.72	1.25	5.77	0.69
0.366	11	27.6	343	4.17	1.12	7.26	0.83
0.229	14	26.9	201	2.76	0.660	8.11	0.95
0.137	17	24.7	230	4.28	0.747	11.1	1.14
0.0915	18.1	22.3	129	2.54	0.423	11.7	1.42
0.0457	22	20.3	111	4.84	0.364	25.8	1.78

^aCorrected dpm in polymer = (dpm in polymer measured)/84%, where dpm in polymer = (cpm observed × 100)/% efficiency.

^bMoles M = (gm. polymer used for counting)/194.1.

^cMoles I = (dpm in polymer corrected)/sp. activity of AIBN-³H. Specific activity of AIBN-³H is 3.047 × 10⁹ dpm/mole.

^d $\bar{M}_n$ = (194.1)(moles M)/(moles I).

^eIntrinsic viscosities measured in MIBK at 30°.

Figure 4. Intrinsic Viscosity in MIBK at 30° for Poly-PFS vs. Molecular Weight: $\circ$ Data obtained by osmometry; $\square$ Data obtained using tritiated AIBN and assuming that termination is entirely by combination.

Figure 4 yields the equations

$$[\eta] = 4.37 \times 10^{-5} \bar{M}_n^{0.736}, \text{ or, } \bar{M}_n = 8.50 \times 10^5 [\eta]^{1.36} \quad (48)$$

Methyl isobutyl ketone (MIBK) is nearly a θ solvent at 30° for poly-PFS and is convenient for osmometry and viscosity measurements. The number-average degree of polymerization, $\bar{P}_n$, of poly-PFS is higher than that of polystyrene by about three times at 60° to about 13 times at 129° (see Figure 3). This observation can be explained if the chain transfer to monomer for PFS is of minor importance in the chain termination step.⁴⁵

The Polymerization of PFS Initiated by AIBN at Different Temperatures. Tables 3, 4 and 5 give data for the AIBN-initiated polymerization of PFS at 60° , 30° and 40°C , respectively. Figures 5, 7 and 9 show these data plotted in the form of Equation 10; the slopes of the lines yield values of $2k_d f / \delta^2$ (see the second column of Table 6). Figures 8 and 10 show the data at 30° and 40° plotted in the form of Equation 13; the slopes of the lines yield values of $\delta^2 / 2[M]^2$, and values of δ^2 can be calculated using known values of $[M]$. The values of δ^2 calculated in this way are given in Table 7 for 30° and 40° . An alternate way to calculate δ^2 is provided by the so-called molecular weight.⁴⁶ Since termination is by combination, the kinetic chain length, ν , equals $\bar{P}/2$, and since $\nu = R_p / R_i$ ⁴⁷

$$R_i = 2R_p / \bar{P} = 2k_d f [I] \quad (49)$$

The data in Table 3 can be plotted in the form $2R_p / \bar{P}$ vs. $[AIBN]$ and

the result is a straight line with a slope equal to $2k_d f$. For example, in pure PFS, the slope gives $R_i = 11.8 \times 10^{-6} [\text{AIBN}] \text{ sec}^{-1}$. If the value of $1.13 \times 10^{-5} \text{ sec}^{-1}$ is taken for k_d at 60° ,³⁷ then a value of f for AIBN can be calculated from these slopes; for example, in pure PFS, f is found to be 0.52. This is in satisfactory agreement with other values in the literature; for example, the f value of AIBN in *p*-fluorostyrene, obtained by inhibitor method, is 0.55.⁴⁸ Table 6 gives values of f for AIBN calculated by this method for mixtures of PFS and a number of solvents. By using these values of f , and the literature value of k_d ,³⁷ apparent values of δ^2 can be calculated. These data are shown in the last column of Table 6. The solvent dependence of δ^2 is quite clearly observed for PFS as well as styrene.^{49,50}

In the absence of solvent, if the % polymerization is low, Equation 13 may be simplified as

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_p + C_M + C_I \frac{[I]}{[M]} \quad (50)$$

If C_I is not negligible, a plot of $(\bar{P} \times R_p)^{-1}$ vs. R_p^{-1} should give a straight line with a slope equal to $\{C_M + C_I \frac{[I]}{[M]}\}$. This relationship can be easily seen from a transformation of Equation 50:

$$\frac{1}{\bar{P} \times R_p} = \{C_M + C_I \frac{[I]}{[M]}\} \frac{1}{R_p} + \frac{\delta^2}{2[M]^2} \quad (50a)$$

Figure 6 is a graph of Equation 50a for the polymerization of PFS initiated by AIBN by using the data in Table 3. A straight line

relationship is observed. Least square treatment yields slope = -4.54×10^{-6} ; intercept = 6.56. Since a negative slope is not allowed by theory, it is concluded that the slope is essentially equal to zero within the limits of the experimental error. (The standard deviation in the slope is $\pm 6.56 \times 10^{-6}$ and in the intercept is $\pm 2.61 \times 10^{-1}$. The probable error in the slope is 4.42×10^{-6} and in the intercept is 1.76×10^{-1} . The maximum slope allowed is 2×10^{-6} . If $C_I = 0$, then C_M is ~40 times smaller than that of styrene). This means that both C_M and C_I must be zero also. In contrast with PFS, styrene has a C_M of 8×10^{-5} at 60° .³² If the rate constants in $\delta^2 = k_p^2/(2k_t)$ are expressed in terms of Arrhenius type equations, then we obtain:^{57c}

$$k_p^2/(2k_t) = (A_p^2/A_t)e^{-(2E_p - E_t)/RT} \quad (51)$$

where A_p , A_t are the collision frequency factors for propagation and termination, respectively, and E_p , E_t are the energy of activation for propagation and termination, respectively. By plotting $\log(1/\delta^2)$ against $1/T$, $2E_p - E_t$ and A_p^2/A_t can be evaluated. Such a plot for AIBN-initiated polymerization of PFS is shown in Figure 11 using the data in Tables 6 and 7. An excellent linear relationship is observed indicating that the two methods employed in the calculation of δ^2 are self-consistent. The following equation is obtained from the least squares fit:

$$1/\delta^2 = 4.01 \times 10^4 \exp(-11,300/RT) \quad (52)$$

Tobolsky and Offenbach⁵² obtained the corresponding equation for styrene:

$$1/\delta^2 = 1.74 \times 10^5 \exp(-12,740/RT) \quad (53)$$

Since in an initiated polymerization, R_p is proportional to $k_p(k_d/k_t)^{0.5}$ (see Equation 10), the observed over-all activation energy, E , can be shown^{30,57c} to be

$$E = (E_p - E_t/2) + E_d/2 \quad (54)$$

where E_d , the activation energy for spontaneous decomposition of the initiator, is about 30 kcal/mole for AIBN or benzoyl peroxide.⁵³ From Equation 52, $E_p - E_t/2 = \frac{11.3}{2} = 5.6$ kcal/mole, and the over-all activation energy for AIBN-initiated polymerization of PFS is therefore $E = 5.6 + \frac{30}{2} = 20.6$ kcal/mole. This value corresponds to a two- to three-fold increase in rate for a 10°C temperature change. The corresponding value of E for styrene is 21.4 kcal/mole. Many other polymerization reactions have E of 20-21 kcal/mole. Note that Equation 52 refers only to the ratio of rate constants $k_p^2/(2k_t)$ and does not include the effect of temperature on the rate of initiation. In photo-polymerization, where the rate of initiation is independent of temperature, Equation 52 represents the complete activation energy.

The value of $1/\delta = k_p/(2k_t)^{0.5}$ gives the polymerizability of the monomer. Comparable values at 60° are PFS, 0.0385; styrene,⁵² 0.0333; methyl methacrylate,³⁸ 0.147; vinyl acetate,⁵⁴ 0.430. A comparison between the reactivities of poly-PFS and polystyryl radicals will be given after the section on absolute rate constants.

Table 3
The Polymerization of PFS Initiated by AIBN at 60°

Third Solvent ^a	[M] ^b	[AIBN] $\times 10^4$	[M][I] ^{0.5}	Time, hr (at 60°)	Convsn. %	R_p, obsd $\times 10^{5c}$	$R_p \times 10^{5d}$	$[\eta]$	$10^4/\bar{P}$
None	6.69	185	0.910	3	17.6	12.0	12.0	0.37	8.80
None	6.44	92.5	0.617	6	24.3	8.25	8.25	0.42	7.43
None	6.36	37.0	0.385	11	26.5	4.91	4.91	0.75	3.37
None	6.42	9.24	0.194	20	24.9	2.53	2.53	1.38	1.47
None	6.60	1.85	0.0898	42	20.0	0.971	0.970	2.69	0.594
None	7.00	185	0.952	1.5	9.20	12.5	12.5	0.40	7.92
None	7.01	92.5	0.674	2	8.84	8.99	8.99	0.49	5.94
None	7.03	37.0	0.427	3	8.22	5.58	5.58		
None	7.10	9.25	0.216	5	6.44	2.62	2.62		
Fluorobenzene	3.56	502	0.799	1	5.46	5.55	5.55		
Fluorobenzene	3.36	185	0.457	5	16.6	3.38	3.38	0.24	15.8
Fluorobenzene	3.21	92.5	0.309	10	24.5	2.49	2.49		
Fluorobenzene	3.09	37.0	0.188	9	31.2	1.66	1.66	0.42	7.43
Fluorobenzene	3.40	9.24	0.103	24	14.6	0.621	0.618	0.83	2.94
THF	3.28	660	0.894	0.5	9.91	10.1	10.1		
THF	3.19	177	0.425	5	25.8	5.26	5.26	0.28	12.9
THF	3.18	88.4	0.299	7	26.2	3.81	3.81	0.32	10.8

Table 3 (Continued)

Third Solvent ^a	[M] ^b	[AIBN] $\times 10^4$	[M][I] ^{0.5}	Time, hr (at 60°)	Convsn. %	$R_{P, \text{obsd}}$ $\times 10^{5c}$	$R_P \times 10^{5d}$	$[\eta]$	$10^4/\bar{P}$
THF	3.30	9.24	0.100	20	19.9	1.01	1.01	0.57	4.89
THF	3.27	3.70	0.0629	30	21.6	0.731	0.728	0.63	4.28
THF	3.35	1.85	0.0455	40	17.0	0.432	0.428	0.70	3.70
Pyridine	3.03	531	0.703	3	34.4	11.7	11.7		
Pyridine	3.19	531	0.735	3	25.9	8.80	8.80		
Pyridine	3.09	177	0.411	6	31.2	5.41	5.41		
Pyridine	3.30	88.4	0.310	4	19.6	4.99	4.99		
Pyridine	3.44	9.24	0.104	20	12.1	0.614	0.611		
Pyridine	3.37	1.85	0.0458	40	15.9	0.405	0.401		

^aSolutions consist of PFS and AIBN plus the third component listed. Solvents are 50% by volume.

^bPFS in moles per liter--the molarities shown are average molarities which have been corrected for % conversion.

^cObserved rate of polymerization in $M \text{ sec}^{-1}$.

^d $R_P = [R_{P, \text{obsd}}^2 - R_{P, \text{th}}^2]^{\frac{1}{2}}$; $R_{P, \text{th}} = 0.570 \times 10^{-6} M \text{ sec}^{-1}$.

Table 4
The Polymerization of PFS Initiated by AIBN at 30°

Third Solvent ^a	$\frac{[AIBN]}{\times 10^4}$	$[M][I]^{0.5}$	Time, hr (at 30°)	Convsn. %	$R_p \times 10^5$ ^b	$[\eta]$	$10^4/\bar{P}$ ^c
None	177	0.968	7.5	3.50	0.950	0.74	3.42
None	177	0.968	9	5.06	1.14	0.67	3.90
None	44.2	0.484	13	3.13	0.490	1.29	1.61
None	17.7	0.303	13	2.29	0.358	----	----
Fluorobenzene	177	0.484	8	3.56	0.453	0.45	6.75
Fluorobenzene	177	0.484	8	4.62	0.588	0.37	8.95
Fluorobenzene	44.2	0.242	14.5	4.13	0.289	0.59	4.67
Fluorobenzene	17.7	0.153	20.5	5.16	0.256	0.96	2.41
Benzonitrile	177	0.484	8	6.66	0.847	0.60	4.67
Benzonitrile	88.4	0.342	11	7.29	0.674	0.64	4.18
Benzonitrile	44.2	0.242	14.5	4.85	0.340	1.29	1.62
Benzonitrile	17.7	0.153	20.5	5.54	0.275	1.65	1.15
Benzotrifluoride	177	0.484	8	6.00	0.763	0.30	12.0
Benzotrifluoride	88.4	0.342	11	4.75	0.439	0.43	7.14
Benzotrifluoride	17.7	0.153	20.5	3.95	0.197	0.86	2.81

Footnotes to Table 4

^aSolutions consist of PFS and AIBN plus the third component listed. Solvents are 50% by volume, i.e., $[M] = 3.64 \text{ M}$ for all 50:50 mixtures.

^bCorrected for thermal polymerization rate.

^cCalculated from Equation 48.

Table 5
The Polymerization of PFS Initiated by AIBN at 40°^a

$[AIBN]$ $\times 10^4$	$[M][I]^{0.5}$	Time, hr (at 40°)	Convsn. %	$R_p \times 10^5$	$[\eta]$	$10^4/\bar{P}$
177	0.958	3.5	4.78	2.78	0.48	6.28
177	0.958	3	4.48	3.04	----	----
88.4	0.677	5	5.06	2.06	0.65	4.14
44.2	0.479	7	4.38	1.27	0.94	2.49
17.7	0.303	9	3.45	0.779	1.61	1.19

^aSee footnotes under Table 3.

Table 6
The Polymerization of PFS Initiated by AIBN at 60°

Solvent ^a	$(2k_d f / \delta^2) \times 10^8{}^b$	f^c	Apparent $\delta^2{}^d$
None	1.74	0.52	675
Fluorobenzene	0.548	0.25 ^e	1030 ^e
THF	1.42	0.28 ^e	446 ^e
Pyridine	1.74		
Styrene		0.55 ^f	
MMA		0.50 ^g	

^a Solvents are 50% by volume.

^b Calculated from the slopes of graphs like Figure 5.

^c Calculated from plots of Equation 49 and the value 1.13×10^{-5} for k_d .

^d Calculated from column 2 and 3.

^e Corrected for chain transfer and high conversion.

^f Calculated from the equation $R_i = 2R_p(1/\bar{P} - C_M)$, where C_M is the average of the transfer constants for styrene and PFS; i.e., 4×10^{-5} . Values of $\bar{P}$ were measured for the copolymer by osmometry and the same technique as described in the Experimental Section for Poly-PFS.

^g Calculated by assuming termination occurs 50% by combination.

Table 7

The Polymerization of PFS Initiated by AIBN at 30° and 40°

Solvent ^a	δ^2 ^b	
	30°	40°
None	3710	2070
Fluorobenzene	4000	----
Benzonitrile	1530	----
Benzotrifluoride	4160	----

^aSolvents are 50% by volume.

^bCalculated from the slopes of Figure 8 and 10.

Figure 5. Graph of Equation 10 for the AIBN-Initiated Polymerization of PFS at 60°. Solvents (50% by volume) are coded as follows: ●, None; ▲, THF; ■, Fluorobenzene. Data for Pyridine as Solvent are not shown; they lie very near the Line for Pure PFS.

Figure 6. Graph of $(\bar{P} \times R_p)^{-1}$ vs. R_p^{-1} for the Polymerization of PFS Initiated by AIBN (●), and by AIBN-³H (▲), 60°.

Figure 7. Graph of Equation 10 for the AIBN-Initiated Polymerization of PFS at 30°. Solvents (50% by volume) are coded as follows: ○, None; ▲, Fluorobenzene; ■, Benzotrifluoride; ◆, Benzonitrile.

Figure 8. Graph of Equation 13 for the AIBN-Initiated Polymerization of PFS at 30°. Solvents (50% by volume) are coded as follows: $\circ$, None; $\blacktriangle$, Fluorobenzene; $\blacksquare$, Benzotrifluoride; $\blacklozenge$, Benzonitrile.

Figure 9. Graph of Equation 10 for the AIBN-Initiated Polymerization of PFS at 40°.

Figure 10. Graph of Equation 13 for the AIBN-Initiated Polymerization of PFS at 40°.

Figure 11. Graph of $\log (1/\delta^2)$ vs. $1/T$ for the AIBN-Initiated Polymerization of PFS in Bulk.

Data on the Thermal Polymerization of PFS in Solvents at

60°.

Transfer Constants in Thermal Polymerization. Thermal polymerization of PFS was carried out in a number of solvents in which poly-PFS is soluble. Table 8 gives the data obtained. In addition, transfer to some non-solvents such as toluene and benzene was studied using THF and/or fluorobenzene as a cosolvent, and the results are shown in Table 9. Equation 55 was used to calculate transfer constants⁵⁵ in the presence of a cosolvent such as THF.

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_P + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_{THF} \frac{[THF]}{[M]} \quad (55)$$

The terms due to transfer to PFS monomer, C_M , and to AIBN, $C_I[I]/[M]$, have been taken as approximately zero and S is a variable solvent. Comparable data for styrene for the solvents THF, methyl isobutyl ketone (MIBK), methyl isopropyl ketone (MIPK), fluorobenzene, benzonitrile, benzotrifluoride, and hexafluorobenzene were also obtained as shown in Table 10. It should be noted that in some cases the samples were prepared in the air and the R_P/R_P^0 ratios are larger than 5 where $R_P^0 = R_{P,th}[M]/[M]_0$, $[M]_0$ and $[M]$ are the molar concentrations of pure monomer and diluted monomer and R_P is the observed rate of polymerization. It is necessary to plot $\{\frac{1}{\bar{P}} - \frac{\delta^2}{2[M]^2} R_P - C_M\}$ against $[S]/[M]$ in order to obtain the correct values of C_S for these systems.⁵⁶ In the cases where R_P/R_P^0 is smaller than 5, the Mayo plot of $1/\bar{P}$ vs. $[S]/[M]$ gives the correct values of C_S . Figures 12-15 show plots of Equation 55 in the form necessary to determine the transfer constants. Table 11 compares

the transfer constants for PFS with data for styrene. As Table 11 shows, plots like Figure 13 and 14, which are corrected for enhanced rates of polymerization,⁵⁶ gave the same transfer constant as did the normal Mayo plot for all transfer agents except MIBK.

Selectivity. The data of Table 11 show that the radical from PFS is approximately as selective toward benzylic hydrogens as is the polystyryl radical. The reactivity of primary- secondary-tertiary hydrogens (per hydrogen) in the series toluene-ethylbenzene-cumene is 1 : 6.7 : 17 for PFS and 1 : 7.8 : 20 for styrene. Transfer constants can be rationalized in terms of dipolar forms for the resonance structures of the transition states.⁴⁷ As expected, the PFS radical is much less able to bear positive charge as required in dipolar form II than is the polystyryl radical.

Thus the polystyryl radical has an enhanced transfer constant to the ketones relative to toluene, whereas the reverse is true of the radical from PFS.

Order in Monomer for PFS and Styrene. Figures 16 and 17 are the graphs of $\log R_{p,th}$ vs. $\log [M]$ for PFS and styrene, respectively, using the data from Tables 8 and 10. The slopes of Figures 16 and 17 are listed in Table 12. It is seen that the orders in styrene monomer determined in substituted benzene solvents lie close to 5/2 (average 2.3).

On the other hand, the corresponding orders in PFS are all less than 2, ranging from 1.57 for fluorobenzene to 1.93 for benzotrifluoride (average 1.8).

Difficulties in Solvent Purification. The peroxide tests (described by Fieser¹⁰²) showed that THF, MIBK and MIPK form peroxides very easily and rapidly on standing. The non-oxygen containing solvents like fluorobenzene, benzonitrile, benzotrifluoride, benzene, toluene, ethylbenzene, cumene, hexafluorobenzene form peroxides more slowly. Therefore, the previous data on thermal polymerization of PFS in THF and ketones might be in error since the solvents used were exposed to air while ampoules were filled. In order to check these data, the thermal polymerization of PFS in THF and ketones were repeated with great caution. The solvent and the monomer were distilled (in the presence of nitrogen) into the calibrated ampoules and sealed on a vacuum line. The new data for these solvents are given in Table 8. The new ratios of R_p/R_p^0 are much closer to 1 and in most cases are less than 5. We believe that all of these values should be much closer to unity, and probably all of them should be less than 1. That is, it is unlikely that any solvents increase the fractional rate of thermal polymerization.^{103,131-2} (Note that the R_p/R_p^0 ratio used here is equivalent to the ratio of fractional rate of polymerization in solvent to that in no solvent case). The reason the values are larger than 1 is probably due to the presence of impurities such as peroxides in the solvents studied. (The slopes of the plot of $\log R_p$ vs. $\log [M]$ for MIPK and MIBK are still too low, see Figure 16). On the other hand,

both the orders in monomer (Figure 16) and the value of the transfer constants to THF, MIBK and MIPK are not altered significantly. Therefore, the data reported¹³ for R_p/R_p^0 for THF, MIBK and MIPK must be corrected but the values of C_s and monomer orders are essentially unchanged (see Tables 11 and 12). It is believed that the corresponding data reported in Table 10 on the thermal polymerization of styrene in solvents, especially THF, might be in error also. In the polymerization of PFS in cumene where either THF¹³ or fluorobenzene was used as cosolvent (see Table 9), the transfer constants obtained for cumene agreed excellently.¹³ However, only in the cases where THF (but not fluorobenzene) was used as cosolvent, were the R_p/R_p^0 ratios observed much greater than 1. Apparently the purity of cumene itself does not play a major role in the enhancement of the over-all rate. This observation could be true also for other aromatic solvents like benzene and ethylbenzene in the cosolvent systems studied since these solvents do not peroxidize rapidly. It should be noted that the transfer constant of THF from the AIBN-initiated runs is found to be 1.61×10^{-4} in excellent agreement with 1.53×10^{-4} obtained from the uncatalyzed runs.¹³ This also indicates that peroxide impurities in the THF did not significantly affect the C_s , since they would contribute negligibly to the over-all rate in the AIBN-initiated polymerization.

Activation Energy of Thermal Initiation. The activation energy for the thermal initiation can be estimated as follows.⁵⁷ Assume that k_p and k_t have the same value for both the thermal and the initiated polymerization. If the rate of thermal initiation is given

as: $R_{i,th} = k_{i,th}[M]^a$, where a is a constant, then Equation 10 becomes

$$R_{p,th} = [M] \frac{\{k_{i,th}[M]^a\}^{0.5}}{\delta} = \frac{k_{i,th}^{0.5}}{\delta} [M]^{1+a/2} \quad (56)$$

Thus in a thermal polymerization, $R_{p,th}$ is proportional to $k_p(k_{i,th}/k_t)^{0.5}$, and the observed over-all activation energy, E_{th} , can be shown^{30,57b} to be

$$E_{th} = (E_p - E_t/2) + E_{i,th}/2 \quad (57)$$

where $E_{i,th}$ is the activation energy for the thermal initiation. The over-all activation energy, E_{th} , obtained for thermal polymerization of PFS in bulk is 16.8 kcal/mole and the $(E_p - E_t/2)$ value obtained from the AIBN-initiated polymerization of PFS (see previous sections) is 5.6 kcal/mole. Therefore, from Equation 57 the $E_{i,th}$ value for PFS is $2 \times (16.8 - 5.6) = 22$ kcal/mole. Another method of calculating $E_{i,th}$ is provided by a plot of $\log \bar{P}_n$ vs. $1/T$ as in Figure 3. Since all the transfer reactions are absent in the thermal polymerization of PFS ($C_M = 0$), Equation 46 is applicable. From the slope of Figure 3, $E_p - E_t/2 - E_{i,th}/2 = -4.2$. Substituting in the value of $(E_p - E_t/2) = 5.6$ yields $E_{i,th} = 20$ kcal/mole. Thus two values of $E_{i,th}$ are in good agreement. The literature values of $E_{i,th}$, E_{th} and E for other vinyl monomers are given in Table 13.

The Mechanism of Thermal Initiation. The mechanism for the spontaneous initiation of polymerization of styrene which has received the most support is that first postulated by Mayo.^{109,110} It involves

a reversible Diels-Alder condensation of two styrenes to form an adduct, AH, which then transfers a hydrogen to another styrene molecule:

Scheme I

Mayo's mechanism (Scheme I) is substantiated by the following observations.

- (1) 1-Phenyltetraline, as well as other derivatives, are isolated in a substantial yield from styrene heated at 130° for 1 hr.⁵¹
- (2) The over-all rate of thermal polymerization is 2.5 order in styrene as required for a termolecular initiation-mechanism.^{28,118}
- (3) The kinetic isotope effect studies^{27,118,121-2,127-8} have confirmed the involvement of ortho hydrogen atoms in the initiation reaction.
- (4) Mayo's mechanism has been shown to be consistent with the observed activation energy for thermal initiation of styrene (29 kcal/mole).^{109,110}
- (5) Statistical calculations¹³³⁻⁴ indicate that small diradicals could not propagate to give high-molecular-weight polymer, because they would be very prone to undergo cyclization reactions. A mechanism involving initial formation of diradicals which then undergo transfer to monomer

to form monoradicals was also calculated to be improbable.²⁸ (6) The kinetic studies on the related monomers 2-vinylfuran and 2-vinylthiophene^{58,59} have suggested that the thermal initiation for these monomers also is a termolecular process in support of Mayo's mechanism. Also a rearranged Diels-Alder type dimer of the structure similar to 1-phenyltetraline was isolated for each of these two monomers.

These findings suggest that the Mayo mechanism may be valid for other vinyl monomers such as 2-vinylfuran⁵⁹ and 2-vinylthiophene⁵⁸ as well as styrene. However, a recent study by Brown¹¹⁷ indicates that a more extended reaction scheme for the thermal polymerization of styrene (Scheme II) may be needed. Brown¹¹⁷ observed that the principal dimeric products isolated from the heated styrene are cis- and trans-1,2-diphenylcyclobutane in a 1:2 ratio and that 1-phenyltetraline is not the major dimeric product as claimed by Müller.⁵¹ Therefore, Brown¹¹⁷ proposed a more extended scheme for styrene (Scheme II) in which the Diels-Alder dimer (AH) is the common intermediate, giving rise to cyclobutanes (either directly by ring contraction or via the diradical intermediate) and other dimeric products such as 1-phenyltetraline:

Scheme II

We believe that the differences in the behavior of PFS and styrene suggest that these 2 similar monomers have important differences in their mechanisms of thermal initiation. We propose the following scheme (Scheme III) for the thermal polymerization of PFS:

Scheme III

This scheme is supported by the following facts and arguments: (1) The thermal rate of PFS polymerization is similar to that of styrene;

therefore, in the PFS polymerization there must be a step (or steps) in which monomer disappears at a rate comparable to that of styrene. We do not believe that a fluorine atom could be transferred from AF the same rate as a hydrogen atom from AH since a C-F bond is stronger than a corresponding C-H bond. The arguments for a stronger C-F bond are as follows: (a) The bond dissociation energy (BDE) for an "allylic" C-H bond (i.e., $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{H}$ bond) is 85 kcal at 25°C .¹⁰⁸ The corresponding BDE for an "allylic" C-F bond is not available in the literature. However, an estimation may be made in the following way: The BDE values for $n\text{-C}_3\text{H}_7\text{-H}$ bond and $n\text{-C}_3\text{H}_7\text{-F}$ bond are 98 kcal and 106 kcal at 25°C ,¹⁰⁸ respectively. The difference between a $n\text{-propyl-H}$ bond and an "allylic" C-H bond is $98 - 85 = 13$ kcal. If the difference between a $n\text{-propyl-F}$ and an "allylic" C-F bond is the same as that between a $n\text{-propyl-H}$ bond and an "allylic" C-H bond, then the BDE of an "allylic" C-F bond is $106 - 13 = 93$ kcal at 25°C . Since the BDE value for a $\text{CH}_3\text{-F}$ bond is 108 kcal¹⁰⁸ compared to 104 kcal for a corresponding $\text{CH}_3\text{-H}$ bond,¹⁰⁸ the allylic radical resonance energy is then $108 - 93 = 15$ kcal for fluorine compound and $104 - 85 = 19$ kcal for the corresponding hydrogen compound. Therefore, the ΔH value needed for breaking an allylic C-F bond is $93 - 15 = 78$ kcal; for an allylic C-H bond, $\Delta\text{H} = 85 - 19 = 66$ kcal. Thus it takes a considerably higher energy to dissociate an allylic C-F bond than does a corresponding C-H bond; (b) Benson¹²⁹ estimated that the activation energies for hydrogen atom abstractions by organic radicals from organic molecules in exothermic reactions are all about 8 ± 2 kcal and are not too sensitive to the over-all exothermicity of the reaction. In contrast, the atoms of fluorine appear never to be

abstracted or to shift in cyclopropane pyrolysis, and a lower limit for such abstractions is estimated to be about 16 kcal/mole; (c) It is observed that the transfer constant to PFS is negligible compared to that of styrene at 60°. ¹³ Also, the transfer constant to solvents by poly-PFS is in the following order: benzene > fluorobenzene > hexafluorobenzene; (d) There are cases where perfluorinated compounds are less resistant to oxidation than their hydrocarbon analog. ¹²⁴ For example, polyperfluorophenylene is markedly less resistant to oxidation at temperatures up to 500°C than its hydrocarbon analog. However, if the polyperfluorophenylene is pretreated at 400°C for 1 hour, ¹³⁵ the oxidative stability increases considerably and compares favorably with the stability of the poly-p-phenylenes in air. On the other hand, poly-PFS is remarkably more stable thermally than polystyrene. It is also more resistant to oxidation than polystyrene. ⁵ Apparently, the generality of such oxidation stability is not known, it may still be safe to assume that a C-F bond is stronger than a corresponding C-H bond). Therefore, the path A should be much slower than the analogous path for styrene. The path C should be slow also since the transfer constant to PFS is zero. The remaining path which is primarily responsible for the monomer disappearance (chain growth) would be path B. (2) The average order for polymerization of PFS using several substituted benzenes as solvents was close to 2 instead of 2.5 as for styrene (Table 12). This implies that a bimolecular initiation mechanism is operative, and the step which forms either the diradical (I) or the Diels-Alder adduct (AF) would be rate-determining. Again, we do not

believe a fluorine atom would be transferred in path A so fast that the formation of the adduct AF becomes the rate-determining step. Instead, the formation of the diradical (I) would be more likely to be rate-determining, and it would be able to add monomer at a reasonably fast rate so that the over-all rate is second order in PFS. (3) We believe that the diradical (I) formed in the PFS system would be more reactive than that formed in the styrene system due to inhibition of resonance by the fluorine atoms in the ring,⁵ and that the former would be more extended than the latter due to dipole-dipole repulsion of both ends. The effect is that the PFS diradical would have a reduced rate of intramolecular cyclization.¹³³ (It can be shown (see Appendix III) that, in a diradical polymerization, a first-order termination process such as intramolecular cyclization would raise the over-all order for the polymerization to 3. If, on the other hand, the rate of termination is bimolecular as in the case of monoradical-initiated polymerization, the over-all rate of thermal polymerization will be second-order in monomer. Also, this bimolecular diradical mechanism would yield the equations identical to those found in monoradical polymerization such as Equations 13 and 57). (4) PFS has an activation energy of thermal initiation which is much lower than that of styrene (Table 13). This may be explained also if the PFS polymerization follows a different mechanism from that of styrene. We believe that an activation energy of about 30 kcal/mole may be required for a monomer undergoing termolecular initiation, and that the calculated $E_{i,th}$ value for PFS, α -vinylnaphthalene or acenaphthylene is either too low or too high

to allow a Mayo type termolecular mechanism to be significant in the thermal initiation reactions of these monomers. Aso *et al.*^{58,59} suggest that both 2-vinylfuran and 2-vinylthiophene follow Mayo mechanism, and these monomers have an activation energy of thermal initiation of about 30 kcal/mole very near that for styrene. On the other hand, Gelhaar and Ueberreiter,⁴⁵ in support of Kirchner and Patat's hypothesis,⁶⁷ proposed that the thermal polymerization of acenaphthylene is initiated by a bimolecular mechanism which involves the hydrogen transfer between two monomer molecules yielding two monoradicals. For this monomer, the activation energy $E_{i,th}$ is extremely high (38 kcal/mole) as a result of steric hinderance.⁴⁵ (5) No identification or isolation of any Diels-Alder type dimer (e.g., AH or AF) and its derivatives has yet been reported. However, all the dimers isolated so far for the thermal dimerization of fluorinated olefins in non-polymer systems are of cyclobutane structure.¹¹³⁻⁵ α,β,β -Trifluorostyrene has a strong tendency to thermally dimerize,¹³⁶ yielding a dimer of cyclobutane structure.¹³⁶⁻⁷ This dimerization process competes with high polymer formation even in the presence of either benzoyl peroxide or *t*-butyl perbenzoate.¹³⁶ Dimers of similar cyclobutane structure have been observed with tetrafluoroethylene,¹³⁸ chlorotrifluoroethylene,¹³⁹ and 1,1-dichloro-2,2-difluoroethylene also.¹³⁹ Under pressure, perfluorostyrene also tends to dimerize,¹²⁴ yielding two dimers presumably of the cyclobutane structure. In addition, the dimerization of acrylonitrile was also shown to give 1,2-dicyanocyclobutane via a diradical intermediate.¹¹² The failure to isolate a Diels-Alder dimer for the

fluorinated olefins suggests that path A in Scheme III may be of minor importance in the thermal polymerization of these olefins. A direct examination of the product distribution of the dimers and the trimers of PFS would be necessary to clarify this.

Table 8

Thermal Polymerization of PFS in Solvents at 60°C

[S]/[M]	[M]	Time, hr (at 60°)	Convsn. %	R_p/R_p^0 ^a	$10^5/\bar{P}$ ^b	$[\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p] \times 10^4$ ^c
0	7.33	163	4.74	No Solvent (1.00)	2.83	0

THF						
5.01	1.83	40	3.73	13.3	101	9.77
8.34	1.22	46	3.22	15.0	120	11.6
11.7	0.916	49.5	3.98	23.0	187	18.1
15.0	0.814	49.5	4.10	26.6	235	22.8
3.36 ^d	2.44	38	0.921	2.60	65.6	
3.36 ^d	2.44	50	1.33	2.85	57.9	
5.01 ^d	1.83	50	1.18	3.38	84.8	
8.34 ^d	1.22	50	1.08	4.64	137	

Fluorobenzene						
1.45	3.66	428	13.5	2.25	3.99	
2.92	2.44	408	10.2	2.68	5.91	
4.36	1.83	450	4.21	1.34	8.64	
5.84	1.47	552	10.7	3.45	9.01	

Table 8 (Continued)

[S]/[M]	[M]	Time, hr (at 60°)	Conv., %	R_p/R_p^0 ^a	$10^5/\bar{P}$ ^b	$\left[\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p\right] \times 10^4$ ^c
Methyl Isobutyl Ketone (MIBK)						
2.18	2.44	18	3.83	22.9	8.87	0.0697
3.27	1.83	21	4.83	32.9	12.5	0.0610
5.46	1.22	23	4.97	46.4	18.4	0.180
1.09 ^d	3.66	50	2.30	3.29	7.10	
2.18 ^d	2.44	50	2.36	5.07	10.2	
3.27 ^d	1.83	50	2.22	6.36	13.7	
Methyl Isopropyl Ketone (MIPK)						
3.82	1.83	20	3.01	21.5	50.8	4.32
6.37	1.22	26	5.14	42.5	71.9	5.69
7.65	1.05	26	5.38	51.6	104	8.58
8.92	0.916	27	5.01	53.1	113	9.46
1.27 ^d	3.66	52	2.06	2.84	20.7	
3.82 ^d	1.83	52	1.97	5.41	53.8	
6.37 ^d	1.22	52	2.10	8.67	86.0	
Benzonitrile						
1.34	3.67	101	4.26	3.00	1.75	
5.35	1.47	316	8.54	4.80	2.50	
6.68	1.22	367	7.03	4.12	2.53	

Table 8 (Continued)

[S]/[M]	[M]	Time, hr (at 60°)	Convsn. %	R_p/R_p^o ^a	$10^5/\bar{P}$ ^b	$[\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p] \times 10^4$ ^c
Benzotrifluoride						
1.11	3.67	216	2.46	0.813	2.61	
2.22	2.44	269	2.79	1.12	3.63	
5.55	1.22	367	2.76	1.61	----	
5.55	1.22	367	2.27	1.33	5.41	
Hexafluorobenzene						
1.19	3.67	192	3.13	1.16	----	
1.19	3.67	192	3.80	1.41	3.14	
4.76	1.47	355	2.65	1.33	----	
5.95	1.22	355	1.17	0.708	5.73	
8.33	0.916	355	1.65	1.33	7.58	

^a $R_p^o = R_{p,th}[M]/7.33$ where $R_{p,th} = 0.0280\%/hr$ for pure PFS at 60°, R_p is the observed rate of polymerization in % mole per hour.

^b Calculated by Equation 48.

^c Calculated by assuming $C_M = 0$ and $\delta^2 = 446$ for THF and $\delta^2 = 675$ for MIBK and MIPK solutions.

^d The solvent and the monomer were distilled directly (in the presence of nitrogen) into the calibrated ampoules instead of transfer by pipette in the air.

Table 9

Thermal Polymerization of PFS in Mixed Solvents Consisting of THF and Third Component

[S]/[M]	[THF]/[M]	[M]	Time, hr (at 60°)	Convsn. %	R_P/R_P^0 ^a	$\left\{ \frac{1}{P} - C_{THF} \frac{[THF]}{[M]} \right\}$ $\times 10^4$ ^b	$\left\{ \frac{1}{P} - C_M - \frac{\delta^2}{2[M]^2} R_P - C_{THF} \frac{[THF]}{[M]} \right\}$ $\times 10^4$ ^c
No Solvent							
0	0	7.33	163	4.74		0.283	
Cumene							
0.327	3.36	2.20	25	3.06	14.6	2.51	2.16
0.490	5.03	1.63	35	4.42	20.2	3.45	2.95
0.655	3.36	2.00	40	3.75	12.3	4.82	4.52
0.490	4.37 ^d	1.63	45	2.94	10.5	4.35	
0.490	4.37 ^d	1.63	75	1.02	2.19	3.31	
0.980	4.37 ^d	1.47	65	2.16	5.91	7.41	
0.980	4.37 ^d	1.47	65	1.17	3.21	6.80	
Ethylbenzene							
0.371	3.36	2.20	22	3.72	20.1	1.90	1.47
0.557	5.03	1.63	23	3.89	27.1	3.75	2.77
0.834	5.03	1.54	48	5.51	19.5	5.17	4.71
Toluene							
0.428	3.36	2.20	18	4.01	26.5	1.16	0.51
0.642	10.1	0.977	46	9.21	53.6	1.90	0.58

Table 9 (Continued)

[S]/[M]	[THF]/[M]	[M]	Time, hr (at 60°)	Convsn. %	R_p/R_p^0 ^a	$\left\{ \frac{1}{P} - C_{THF} \frac{[THF]}{[M]} \right\}$ $\times 10^4$ ^b	$\left\{ \frac{1}{P} - C_M - \frac{\delta^2}{2[M]^2} R_p \right.$ $\left. - C_{THF} \frac{[THF]}{[M]} \right\} \times 10^4$ ^c
0.642	10.1	0.977	35	6.82	52.3	1.90	0.58
1.28	5.02	1.47	24	3.64	27.1	2.87	1.90
Benzene							
1.55	2.92 ^d	1.83	144	0.626	0.207	0.517	
1.55	2.92 ^d	1.83	216	0.563	0.124	1.01	
0.771	1.46 ^d	2.93	367	2.28	0.184	0.173	
0.771	1.46 ^d	2.93	367	3.71	0.301	0.501	
Chlorobenzene							
1.34	4.37 ^d	1.47	202	0.886	0.782	-0.072	
1.34	4.37 ^d	1.47	203	0.809	0.711	-0.132	
0.672	2.19 ^d	2.44	203	1.68	0.888	-0.035	
0.447	0.973 ^d	3.67	202	2.04	0.721	0.060	
Bromobenzene							
1.33	5.84 ^d	1.22	241	4.28	3.38	-0.028	
1.33	5.84 ^d	1.22	241	3.19	2.83	-0.055	
0.664	2.19 ^d	2.44	240.5	4.78	2.14	0.165	

Footnotes to Table 9

^aSee footnote a in Table 8.

^bTransfer constant of THF was taken as 1.54×10^{-4} .

^cCalculated by assuming $C_M = 0$ and $\delta^2 = 446$.

^dFluorobenzene used as the cosolvent rather than THF; its transfer constant was taken as 1.16×10^{-5} .

Table 10
Thermal Polymerization of Styrene in Solvents at 60°C

[S]/[M]	[M]	Time, hr (at 60°)	Convsn. %	R_p/R_p^0 ^a	$10^4/\bar{P}$ ^b	$\left\{\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p\right\} \times 10^4$ ^c
No Solvent						
0	8.67	50	5.00	(1.00)	1.14	0
THF						
1.41	4.35	43	11.0	5.12	3.68	2.15
7.07	1.45	76	15.4	12.2	12.7	10.1
7.89	1.09	95	17.3	14.6	17.0	14.1
Fluorobenzene						
1.23	4.35	236	8.65	0.733	1.19	
3.69	2.18	264	4.74	0.715	1.20	
4.92	1.74	299	4.53	0.758	1.40	
6.15	1.45	323	3.98	0.738	1.35	
MIBK						
1.84	2.90	16	1.70	3.18	2.72	
2.76	2.18	18	1.57	3.47	3.13	
5.52	1.24	84	5.16	4.31	5.37	

Table 10 (Continued)

$[S]/[M]$	$[M]$	Time, hr (at 60°)	Conv. %	R_p/R_p^0 ^a	$10^4/\bar{P}$ ^b	$\{\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p\} \times 10^4$ ^c
MIPK						
2.15	2.90	48	3.07	1.92	5.99	
3.22	2.18	50	2.64	2.10	9.24	
5.37	1.45	92	8.17	5.32	14.9	
5.37	1.45	92	6.06	3.94	13.8	
6.44	1.24	92	4.76	3.64	16.0	
Benzonitrile						
2.25	2.90	261	7.45	0.856	1.11	
4.51	1.74	400	7.16	0.895	1.19	
5.63	1.45	400	6.37	0.952	1.24	
Benzotrifluoride						
0.936	4.35	204	7.10	0.694	-----	
1.87	2.90	361	5.85	0.671	1.27	
3.74	1.74	400	4.55	0.570	1.32	
4.68	1.45	400	4.05	0.605	1.36	
Hexafluorobenzene						
1.01	4.33	193	4.07	0.422	1.87	
1.01	4.33	217	5.16	0.476	1.86	

Table 10 (Continued)

$[S]/[M]$	$[M]$	Time, hr (at 60°)	Convsn. %	R_p/R_p^0 ^a	$10^4/\bar{P}$ ^b	$\left\{ \frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2[M]^2} R_p \right\} \times 10^4$ ^c
2.02	2.89	217	2.32	0.320	2.84	
2.02	2.89	217	2.15	0.296	3.24	

^a $R_p^0 = R_{p,th} \times [M]/8.67$ where $R_{p,th} = 0.10\%/hr$ for pure styrene at 60°. R_p is the observed rate of polymerization in % per hour.

^bIntrinsic viscosities were measured in benzene at 30° and the molecular weights were calculated using Mayo's equation (ref.31).

^cCalculated by assuming $C_M = 8 \times 10^{-5}$ (ref.32) and $\delta^2 = 900$ for pure styrene (ref.33).

Table 11
A Comparison of the Transfer Constants for PFS and Styrene
Toward Several Solvents at 60^{oa}

Solvent	$C_S \times 10^4$	
	THF	Styrene
Tetrahydrofuran (THF)	1.61 ⁱ	1.42(1.86) ^b
Cumene	6.76(6.51) ^{d,h}	1.04 ^c
Ethylbenzene	5.35(5.86) ^d	0.83 ^c
Toluene	1.20(2.25) ^d	0.16 ^c
Benzene	0.296 ^e	0.04 ^c
Methyl Isobutyl Ketone (MIBK)	0.328 ⁱ	0.757 ^b
Methyl Isopropyl Ketone (MIPK)	1.30 ⁱ	2.39 ^b
Fluorobenzene	0.116	0.0384 ^b
Chlorobenzene	~0 ^e	0.133 ^f
Bromobenzene	~0 ^e	1.78 ^g
Benzonitrile	~0	0.0141 ^b
Benzotrifluoride	0.0470	0.0451 ^b
Methanol	0.355	---
Hexafluorobenzene	0.0554	0.813 ^b

^a Figures not in parentheses are obtained from plots like Figure 13 or 14 where R_p/R_p^0 was greater than 5. The numbers in parentheses were determined from the ordinary Mayo plot.

^b Determined in this study. All values are computed from least square fits of Equation 55.

^c Recalculated by Henrici-Olivé (ref.32) from data of Mayo (ref.34).

^d Determined in the presence of the cosolvent THF.

^e Determined in the presence of the cosolvent fluorobenzene.

^f Determined by Misra and Chadha (ref.35).

^g Determined by Kapur (ref.36).

^h Using fluorobenzene instead of THF as cosolvent gives $C = 6.98 \times 10^{-4}$.

ⁱ Measured by distilling solvents and PFS directly into ampoules and sealing on a vacuum line. The values obtained by transferring solvents and PFS in the air are as follows: THF, 1.48(1.54); MIBK, 0.033(0.287); MIPK, 1.09(1.24).

Table 12

The Order in Monomer for Thermal Polymerization of PFS and Styrene
in Solvents, 60°

Solvent	<u>a in $R_{P,th} = K[M]^a$</u>	
	PFS	Styrene
Fluorobenzene	1.54	2.07
Benzonitrile	1.65	1.95
Benzotrifluoride	1.85	2.21
Hexafluorobenzene	1.86	2.92
THF	1.23 ^a	1.24
MIPK	1.00 ^a	1.22
MIBK	1.05 ^a	1.64

^a Measured by distilling solvents and PFS directly into ampoules and sealing on a vacuum line. The values obtained by transferring solvents and PFS in the air are as follows: THF, 1.13; MIPK, 1.18; MIBK, 0.99.

Table 13

The Activation Energies for Thermal and Initiated Polymerization
of Some Vinyl Monomers^a

Monomer	E_{th}	$E_{i,th}$	E	Reference
PFS	16.8	20-22	20.6	This study
Styrene	21.0	28.9	21.4 ^c	Mayo, ref.28
2-Vinylthiophene	15.6	28.2	16.5 ^{d,e}	Aso <u>et al.</u> , ref.58
2-Vinylfuran	17	30.0	17 ^{d,e}	Aso <u>et al.</u> , ref.59
Acenaphthylene	30.9	38 ^f	----	Gelhaar & Ueberreiter, ref.45
α -Vinyl-naphthalene	17.4	22 ^b	21.5 ^c	Loshaek <u>et al.</u> , ref.60
o-Chlorostyrene	17.5	30 ^b	17.5 ^d	Rubens, ref.63
2-Vinylpyridine	20.2	29.4 ^b	20.5 ^{c,g}	Koton, ref.65

^aAll in kcal/mole.

^bEstimated from the equation, $E - E_{th} = (E_i - E_{i,th})/2$ (derived by combining the Equations 54 and 57 and assuming $E_i = E_d = 30$ kcal/mole for AIBN- and benzoyl peroxide initiated polymerization). E_{th} and E are the over-all activation energies for the thermal (uncatalyzed) and the initiated polymerization, respectively. $E_{i,th}$ and E_i are the activation energies of the initiation for the thermal and the initiated polymerization, respectively.

^cInitiated by AIBN.

^dInitiated by benzoyl peroxide.

^eDetermined by Koton, ref.64.

^fEstimated from the slope of the plot of $\log \bar{P}_n$ vs. $1/T$ using Eq.46.

^gBengough obtained $E_p - E_t/2 = 5.5$ kcal/mole (ref.66).

Figure 12. Transfer to Fluorobenzene ($\bullet$), Hexafluorobenzene ($\blacktriangle$), Benzotrifluoride ($\blacksquare$), and Benzonitrile ($\blacklozenge$) by PFS at 60°.

Figure 13. Transfer to THF ($\bullet$), MIPK ($\blacktriangle$), and MIBK ($\blacksquare$) by PFS (filled symbols) and to THF by styrene (open circles).

Figure 14. Transfer to Cumene (●), Ethylbenzene (■), and Toluene (▲) by PFS at 60° in the Presence of the Cosolvent THF.

Figure 15. Transfer to MIPK (●), MIBK (▲), Fluorobenzene (■), Benzonitrile (◆), Hexafluorobenzene (▼), and Benzotrifluoride (X) by Styrene at 60°.

Figure 16. Graph of $\log R_p$ vs. $\log [M]$ for Thermal Polymerization of PFS in Solvents at 60° . Solvents are coded as follows:
 ●, Fluorobenzene; ▲, THF; ■, MIBK; ◆, MIPK;
 ▼, Benzonitrile; X, Hexafluorobenzene; and +, Benzotrifluoride.

Figure 17. Graph of $\log R_p$ vs. $\log [M]$ for Thermal Polymerization of Styrene in Solvents at 60° . Solvents are coded as follows: ●, Fluorobenzene; ▲, THF; ■, MIBK; ◆, MIPK; ▼, Benzonitrile; X, Hexafluorobenzene; and +, Benzo-trifluoride.

The Measurement of the Rate of Initiation for PFS. Two methods were employed in the measurement of the rates of initiation for PFS: the molecular weight method, and the inhibitor method. The molecular weight method,⁴⁶ as already described in the section concerning the AIBN-initiated polymerization of PFS, gave reasonable values of the initiator efficiency, f , for PFS-solvent mixtures (see Table 6). The inhibitor method⁴⁶ involves the measurement of the rate of consumption of an inhibitor which is added to the monomer to prevent polymerization. The rate of removal of inhibitor is proportional to the rate of initiation. However, to determine the proportionality constant, it is necessary to make an assumption regarding the number of free radicals which react with one molecule of inhibitor. If, and only if, each inhibitor molecule stops one free radical chain, the rate of removal of inhibitor is equal to the rate of initiation. When DPPH is used as a radical scavenger⁴⁶ the usual assumption is that one free radical reacts with each DPPH radical, so that the rate of initiation, R_i , is equal to the rate of disappearance of DPPH, R_{DPPH} . Since DPPH is a colored substance it is possible to follow its rates of removal by the rate of disappearance of the color from the solution.⁶⁸ PFS was therefore polymerized photochemically at 80°C in the presence of DPPH, and the disappearance of color followed spectrophotometrically at 520 mμ. Blank runs on DPPH-solvent mixtures were also performed, and small corrections were made to the PFS systems. A typical plot of the disappearance of DPPH in PFS-solvent systems is shown in Figure 18. Note that the

plots of $\log (A_t - A_\infty)$ vs. time give straight lines for all cases (where A_t and A_∞ are the absorbance at time t and at infinite point, respectively) whereas the corresponding plots of $(A_t - A_\infty)$ vs. time always show the deviations from linearity. This observation would suggest that R_{DPPH} is essentially first order with respect to DPPH. In contrast, Tobolsky⁶⁹ found R_{DPPH} to be nearly zero order with respect to DPPH in styrene. The data in Table 14 yield the values of monomer order 1.1, 1.5 and 2.2 (average 1.6) determined in benzonitrile, benzonitrile and fluorobenzene, respectively. This compares with the conclusion made by Tobolsky⁶⁹ from two experiments with styrene in benzene solution that R_{DPPH} is second order with respect to styrene. A first-order dependence of R_{DPPH} on the concentrations of DPPH could be explained in terms of the simple direct attack of DPPH radical on PFS monomer molecule. A dependence of the rate of DPPH removal on the 1.1 to 2.2 order of monomer could be explained in terms of the reaction of DPPH radical with PFS monomer, or with the complex of two PFS molecules or a combination of the two reactions. In the AIBN-initiated polymerization of PFS, DPPH failed to give any induction period at all as shown in Figure 19. Apparently, DPPH is not an "ideal" inhibitor^{66,70} for the polymerization of PFS. However, a preliminary experiment using benzoquinone as inhibitor in the place of DPPH did show an induction period (see Figure 19a). From the length of this induction period, the value of R_i was calculated to be $5.0 \times 10^{-8} \text{ M sec}^{-1}$ at $[\text{AIBN}] = 3.05 \times 10^{-3} \text{ M}$. From the molecular weight method, R_i was

estimated to be $3.5 \times 10^{-8} \text{ M sec}^{-1}$ at the same AIBN concentration. Bengough⁴⁶ studied the rate of initiation for MMA using three different methods. He observed that the value obtained using the inhibitor method is approximately double those obtained by the molecular weight method and radioactive tracer method. Therefore, the results obtained here should be regarded as satisfactory.

The Determination of Radical Lifetime (The Rotating Sector Method). Radical lifetimes were determined by the rotating sector method. As the kinetic chain lifetime is inversely proportional to the rate (Equation 22) it is often possible to adjust conditions so that one obtains a suitable value for the lifetime at a reasonable rate of polymerization. Table 15 shows the data obtained under the optimum conditions. The ratio of the rates measured at different sector speeds, R_p , to those obtained at steady light R_{ps} were calculated, and they are listed in column 5 of Table 15. The flash times, λ , were measured for each sector speed. A sector with $r = 2$ (i.e., the ratio of dark to light area is 2 to 1) was used for all runs. The experimental curves were obtained by plotting R_p/R_{ps} vs. $\log \lambda$ (see the line with circles in Figure 20). Since the dark rates are not negligible, Equations 26-28 were used to construct the theoretical curves. The computed values of R_p/R_{ps} as a function of m and z (see Introduction section) are collected in Table 17, and the theoretical curves were obtained by plotting the computed R_p/R_{ps} vs. $\log m$. The values of radical lifetime, τ , were calculated from the difference between the theoretical and experimental curves, and

Table 14

DPPH Disappearance in PFS-Solvent Mixtures at 80°
(Measured at 520 mμ)^a

Solvent	[M]	$R_{\text{DPPH}} \times 10^4$ corrected ^b	a in $R_{\text{DPPH}} = K[M]^a$ corrected
None	6.87	4.16	----

Benzotrifluoride	5.15	1.85	1.49
	3.44	1.55	
	1.72	0.507	
	0	----	

Benzonitrile	5.15	0.705	1.08
	3.44	0.436	
	1.72	0.216	
	0	----	

Fluorobenzene	5.15	3.87	2.16
	3.44	0.935	
	1.72	0.210	
	0	----	

^a In the presence of $[\text{DPPH}] = 9.79 \times 10^{-5} \text{M}$

^b Rate of disappearance of DPPH corrected for solvent absorption. Rates are calculated from the slopes of the plots of $\log (A_t - A_\infty)$ vs. time where A_t and A_∞ are the absorbance at time t and at infinite point, respectively.

Figure 18. DPPH Disappearance in PFS-PhCN Mixtures at 80°.

○ : 100% PFS; ▲ : 75% PFS; ◆ : 50% PFS; ■ : 25% PFS;
▼ : PhCN Blank.

Figure 19. Graph of % Conversion vs. Time for the Polymerization of PFS in the Presence of $[\text{AIBN}] = 1.77 \times 10^{-2} \text{ M}$.

Concentration of DPPH $\bullet$: $2.24 \times 10^{-5} \text{ M}$,
 $\blacktriangle$: $8.98 \times 10^{-5} \text{ M}$, $\blacksquare$: $18.0 \times 10^{-5} \text{ M}$, $\blacklozenge$: 0 .

Figure 19a. Graph of % Conversion vs. Time for the Polymerization of PFS in the Presence of $[AIBN] = 3.05 \times 10^{-3} M$ and $[Benzoquinone] = 1.14 \times 10^{-3} M$.

the average values are given in the column 6 of Table 15. The values of $k_p/(2k_t)$, calculated from Equation 22 using the known values of τ , may be combined with the previously determined δ^2 values obtained from AIBN experiments. The k_p and $2k_t$ values calculated by this way are listed in Table 16. To serve as a comparison, the corresponding data for the photopolymerization of styrene at 30° were also collected. A comparison of the absolute rate constants for some substituted styrenes is given in Table 18. For styrene, $k_p = 107 \text{ M}^{-1} \text{ sec}^{-1}$ and $2k_t = 1.09 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ are obtained. These values are in excellent agreement with the values reported by Imoto *et al.*:⁴⁸ $k_p = 106 \text{ M}^{-1} \text{ sec}^{-1}$ and $2k_t = 1.08 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. For PFS, $k_p = 195 \text{ M}^{-1} \text{ sec}^{-1}$ and $2k_t = 1.39 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Thus k_p for PFS is about twice that of styrene whereas $2k_t$ is about the same for both monomers. In other words, PFS propagates with greater ease than styrene. Since the propagation reaction involves two reactants, $M\cdot$ and M (see Introduction section), it is not possible from values of k_p alone to decide whether the reactivity of polymer radical $M\cdot$ or that of the monomer M has the greater influence upon k_p . To distinguish between radical and monomer reactivities it is necessary to consider the rates of transfer reactions and copolymerizations.^{55b,73} Since $C_S = k_{tr,S}/k_p$ by definition, the values of $k_{tr,S}$ may be calculated from C_S and k_p . If the difference of reaction temperature (60° for transfer reaction and 30° for photopolymerization) is ignored,⁷⁴ and assessment of radical reactivity can be deduced from the rate of transfer to the same substrate by using the data in Table 11. These values of $k_{tr,S}$

for some hydrocarbons are listed in Table 19, and show that the reactivity in this reaction appears to run parallel to the propagation rate constant, but further information on the separate reactivities of monomer and free radical can be more easily deduced from the copolymerization studies (see p.100).

Table 15
Determination of Average Lifetime of PFS Radical at 30°^a

Solvent	[M]	$\log \lambda^b$	$R_p \times 10^6^b$ (M sec ⁻¹)	R_p/R_{Ps}^b	Average τ (sec)	$k_p/2k_t \times 10^6^c$
None	7.28	----	5.50	1.000	1.83	1.39
		-0.169	3.18	0.578		
		0.137	3.11	0.565		
		0.535	2.85	0.519		
		0.838	2.56	0.465		
		1.140	2.35	0.428		
		1.538	2.19	0.398		
		1.838	2.03	0.369		
		2.140	1.98	0.360		
Benzonitrile	3.64	----	4.67	1.000	1.48	1.90
		0.137	2.60	0.556		
		0.535	2.34	0.501		
		0.838	2.13	0.457		
		1.140	1.94	0.416		
		1.538	1.79	0.383		
		1.838	1.70	0.365		
		2.140	1.64	0.352		
Benzotrifluoride	3.64	----	2.69	1.000	1.77	1.31
		0.137	1.48	0.549		
		0.535	1.33	0.493		
		0.838	1.25	0.466		
		1.140	1.16	0.430		
		1.538	1.03	0.383		
		1.838	0.917	0.341		

Table 15 (Continued)

Solvent	[M]	$\log \lambda^b$	$R_p \times 10^6^b$ (M sec ⁻¹)	R_p/R_{Ps}^b	Average τ (sec)	$k_p/2k_t \times 10^6^c$
Fluorobenzene	3.64	----	2.71	1.000	1.79	1.33
		0.137	1.50	0.552		
		0.535	1.37	0.507		
		0.838	1.26	0.464		
		1.140	1.17	0.430		
		1.538	1.08	0.398		
		1.838	1.02	0.377		
		2.140	0.965	0.356		

^aIn the presence of 3.00×10^{-3} M ACHN as photosensitizer. All solvents are 50% by volume.

^b R_p is the measured rate of photopolymerization under intermittent light ($\bar{r} = 2$). R_{Ps} is the rate observed under steady light. λ is flash time in seconds.

^cCalculated from the Equation $k_p/2k_t = R_p \times \tau/[M]$, where τ is the average lifetime of propagating radicals.

Table 16

The Photopolymerization of PFS at 30°, [ACHN] = 3.00 x 10⁻³ M

Solvent	$R_p \times 10^6$ ^a	τ sec	$\frac{k_p}{2k_t} \times 10^6$	δ^2	k_p ^b	$2k_t \times 10^{-8}$ ^c	$R_i \times 10^8$ ^d	$10^4/\bar{P}$ ^e
None	5.50	1.83	1.39	3710	195	1.39	0.212	2.11
PhCN	4.67	1.48	1.90	1530	346	1.83	0.249	2.47
PhCF ₃	2.69	1.77	1.31	4160	184	1.41	0.227	3.49
PhF	2.71	1.79	1.33	4000	187	1.40	0.222	3.62

^aSee footnote b under Table 15. All solvents are 50% by volume.

^b $k_p = R_p/[M]R_i\tau$ in M⁻¹ sec⁻¹.

^c $2k_t = (R_i \times \tau^2)^{-1}$ in M⁻¹ sec⁻¹.

^d $R_i = \delta^2 \times R_p^2/[M]^2$.

^eCalculated from Equation 48.

Table 17

Theoretical Values of R_p/R_s as a Function of m and z for $r=2$

m	$z = 0$	$z = 0.01$	$z = 0.02$	$z = 0.03$	$z = 0.04$
0.1	0.577	0.577	0.577	0.578	0.578
0.2	0.576	0.576	0.576	0.577	0.577
0.3	0.574	0.575	0.575	0.575	0.575
0.4	0.572	0.573	0.573	0.573	0.573
0.5	0.569	0.570	0.570	0.570	0.571
0.6	0.566	0.567	0.567	0.567	0.568
0.7	0.562	0.564	0.564	0.564	0.565
0.8	0.558	0.560	0.560	0.561	0.561
0.9	0.555	0.556	0.557	0.557	0.557
1.0	0.552	0.553	0.553	0.553	0.553
1.5	0.533	0.533	0.533	0.534	0.534
2.0	0.515	0.515	0.515	0.516	0.516
2.5	0.500	0.500	0.500	0.501	0.501
3.0	0.487	0.487	0.487	0.488	0.489
3.5	0.477	0.477	0.477	0.478	0.478
4.0	0.467	0.468	0.468	0.469	0.470
4.5	0.460	0.460	0.460	0.461	0.462
5.0	0.453	0.453	0.453	0.454	0.455
5.5	0.447	0.447	0.447	0.448	0.449
6.0	0.442	0.442	0.442	0.443	0.444
6.5	0.437	0.437	0.437	0.438	0.440
7.0	0.432	0.433	0.433	0.434	0.435
7.5	0.429	0.429	0.429	0.430	0.432
8.0	0.425	0.425	0.426	0.427	0.428
8.5	0.422	0.422	0.423	0.424	0.425
9.0	0.419	0.419	0.420	0.421	0.422
9.5	0.416	0.416	0.417	0.418	0.420
10	0.413	0.414	0.414	0.416	0.417
20	0.384	0.385	0.386	0.388	0.391

Table 17 (Continued)

m	$z = 0$	$z = 0.01$	$z = 0.02$	$z = 0.03$	$z = 0.04$
30	0.372	0.372	0.374	0.377	0.381
40	0.364	0.365	0.368	0.371	0.376
50	0.360	0.361	0.364	0.368	0.373
60	0.356	0.357	0.361	0.365	0.371
70	0.354	0.355	0.359	0.364	0.369
80	0.352	0.353	0.357	0.362	0.368
90	0.350	0.352	0.356	0.361	0.367
100	0.349	0.3507	0.3552	0.3606	0.3664
200	0.342	0.3454	0.3509	0.3570	0.3632
300	0.340	0.3436	0.3495	0.3558	0.3621
400	0.388	0.3427	0.3488	0.3551	0.3616
500	0.3375	0.3422	0.3484	0.3548	0.3613

Table 18

A Comparison of Absolute Rate Constants for Substituted Styrenes^a

Monomer	k_p	$2k_t \times 10^{-8}$	Reference
PFS	195	1.39	This study
Styrene	107	1.09	This study
	106	1.08	Imoto <u>et al.</u> , ref.48
	26	0.052	Melville, ref.71
	55	0.505	Matheson, ref.25
	73	0.67	Norrish, ref.72
p-Fluorostyrene	112	1.27	Imoto <u>et al.</u> , ref.48
p-Chlorostyrene	150	0.77	Imoto <u>et al.</u> , ref.48
p-Bromostyrene	186	0.46	Imoto <u>et al.</u> , ref.48
p-Cyanostyrene	219	0.35	Imoto <u>et al.</u> , ref.48
p-Methylstyrene	84	0.66	Imoto <u>et al.</u> , ref.48
p-Methoxystyrene	71	0.33	Imoto <u>et al.</u> , ref.48

^aAll values are in $M^{-1} \text{sec}^{-1}$ at 30°C.

Table 19

A Comparison of Radical Reactivities for PFS and Styrene^{a,e}

Monomer	k_p ($M^{-1} \text{ sec}^{-1}$, 30°)	$k_{tr,S}$ ($M^{-1} \text{ sec}^{-1}$ all at 60°) $\times 10^2$		
		Toluene	Ethylbenzene	Cumene
PFS	195	2.34	10.4	13.2
Styrene	107	0.171	0.888	1.11
MMA	251 ^b	42.7 ^c	192 ^c	477 ^d

^a Calculated using the data in Table 11 and the equation $k_{tr,S} = C_S \frac{k_p}{C_S}$. Note that k_p and $k_{tr,S}$ are given at different temperatures.

^b Data of Schulz et al., ref.77.

^c Using the data of Chadha et al. (ref.78) for $C_S = 0.170 \times 10^{-4}$ and 0.766×10^{-4} for toluene and ethylbenzene, respectively.

^d Using the data of Allen et al. (ref.79) for $C_S = 1.9 \times 10^{-4}$ for cumene.

^e The trend is not changed for the $k_{tr,S}$ values at 60° calculated by assuming the following values of the activation energies for propagation: PFS, 7-8 kcal/mole (ref.48); styrene, 7 kcal/mole (ref.48); MMA, 5 kcal/mole (ref.7).

Figure 20. Determination of the Average Lifetime of Poly-PFS Radicals
 —: Calculated for $z = \text{dark rate/steady light rate} = 0.02$
 and $\tau = 1.00$ sec.; — with ●: Calculated for $z = 0.02$
 and $\tau = 1.83$ sec.; ---: Calculated for $z = 0.00$ and
 $\tau = 1.00$ sec.

COPOLYMERIZATION

EXPERIMENTAL SECTION

Copolymerization of PFS and Styrene. Copolymer was isolated by the freeze-dry procedure developed by Lewis and Mayo for styrene¹⁹ since the copolymer is soluble in benzene. Copolymer composition was evaluated using % carbon from elemental analysis in the following way: The fraction styrene in the copolymer, f_1 , is related to the fraction carbon in the polymer, x , the molecular weight of PFS, 194.1, and that of styrene, 104.1, and the fraction of carbon in PFS and styrene, 0.4950 and 0.9226, respectively, by the formula:

$$f_1 = (194.1x - 96.079)/(90.0x - 0.036) \cong 2.157 - 1.067/x$$

Copolymerization of PFS and Methyl Methacrylate. The same procedures were followed in isolating the copolymer. Copolymer composition, however, was determined using ultraviolet spectroscopy. (% carbon analysis would introduce great error due to the closeness of the theoretical values of %C in PFS and MMA: 49.5% vs. 60%). In THF as solvent, the specific absorbance for PFS (in units of absorbance per mole per liter) is $\epsilon = 1.92$ at $\lambda_{\max} = 259 \text{ m}\mu$, and is independent of molecular weight. Beer's law is obeyed. At this wavelength, MMA has $\epsilon = 0.095$. The equation used is $\epsilon = 1.92x + (1-x)(0.095)$ where x is the weight fraction of PFS in the copolymer.

RESULTS AND DISCUSSION

Copolymerization of PFS and Styrene Initiated by AIBN.

Styrene (M_1) and PFS (M_2) were allowed to copolymerize at 60° using AIBN as initiator. Copolymer composition was evaluated using % carbon from elemental analysis. The method of Fineman-Ross¹⁵ was used to evaluate r_1 and r_2 (see Equation 37). Table 20 gives the data; the values of $r_1 = 0.42 \pm 0.01$ and $r_2 = 0.22 \pm 0.06$ are obtained from the Fineman-Ross graph (least square fit of data). These data are compared with values for pentachlorostyrene^{40-1,53} and p-fluorostyrene⁵³ in Table 22. Values of $1/r_1$, which give the rate constant for addition of a styryl radical to these monomers relative to the rate constant for addition to styrene, show that the monomers increase in activity in the order pentachlorostyrene < styrene < p-fluorostyrene < PFS. Using the Equation 41 and 42 and the values of $Q_1 = 1.00$ and $e_1 = -0.80$ for styrene gives $Q_2 = 0.69$ and $e_2 = 0.74$ for PFS. A typical graph for the relationship between copolymer and feed (monomer mixture) compositions is shown in Figure 20a.

The copolymerization was also studied at 60° using AIBN initiation to determine the value of the cross-termination ratio ϕ (see Introduction). Equation 45 was used for calculation. Table 20 gives the data. A value of $\phi = 7.2$ is found, indicating a substantial tendency toward cross-termination.^{7,47}

Copolymerization of PFS and Methyl Methacrylate Initiated

by AIBN. The same procedures were followed in evaluating copolymerization parameters for MMA (M_1) and PFS (M_2). The composition of the copolymer was determined using ultraviolet spectroscopy. Table 21 gives the data. The Fineman-Ross treatment yields $r_1 = 0.99 \pm 0.03$ and $r_2 = 0.91 \pm 0.06$. These data are compared with values of pentachlorostyrene^{40-1,53} and styrene in Table 22. Values of $1/r_1$, which give the rate constant for addition of a poly-MMA radical to these monomers relative to the rate constant for addition to MMA, show that the monomer increase in activity in the order pentachlorostyrene < MMA $\approx$ PFS < styrene. By using $Q_1 = 0.74$ and $e_1 = 0.40$,⁴⁰ the values of $Q_2 = 0.87$ and $e_2 = 0.75$ are obtained for PFS. These values are in fairly satisfactory agreement with 0.69 and 0.74, respectively, obtained from the styrene-PFS copolymerization. Table 21 also gives rate data, and the value of $\phi = 5.3$ is obtained.

Table 23 summarizes the copolymerization behavior of PFS. The average value of e of 0.75 for PFS appears quite reasonable compared with -0.8 for styrene, -0.12 for *p*-fluorostyrene, and 0.52 for pentachlorostyrene.⁵³ The average value of Q of 0.78 for PFS can be compared with 1.00 for styrene, 0.83 for *p*-fluorostyrene, and 0.22 for pentachlorostyrene.⁵³ Alfrey and Ebelke⁴¹ have suggested that the reduced Q value of pentachlorostyrene results from a steric inhibition of resonance due to the *o*-chloro substituents. A similar explanation could be evoked for PFS (Atomic radii in Ångströms are H, 0.28; F, 0.64; Cl, 0.99).⁷⁶

It is usually expected that a large tendency toward alternation of monomers in a copolymer will be reflected in a large value of ρ . The data of Table 23 do not agree with this expectation; the styrene copolymer, which is appreciably alternating, has a rather small ρ value. Table 24 summarizes similar data for the literature. Walling⁴³ found that the ρ for the styrene-diethyl fumarate system was surprisingly low despite the pronounced alternating tendency of the copolymer. Apparently, the radical recombination reaction is far less sensitive to polar factor than is the more activated addition to a double bond.

Combination of r_2 from the copolymerization studies with k_p from the photopolymerization experiments enables us to discuss the relative reactivities (k_{21}) of poly-PFS and polystyryl radicals as shown in Table 23. The difference of reaction temperature (60° for copolymerization and 30° for homopolymerization) is not considered. The order of radical reactivities is the same as that observed in transfer reactions (see Table 19), *i.e.*, styrene < PFS < MMA. Quite obviously it follows from the Q values and the individual rate constants shown in Tables 23 and 19 that the monomer PFS is less reactive than styrene (since the Q value for PFS is smaller than that of styrene, see Table 23), but that the radical is more reactive (for example, the values of $k_{tr,s}$ for PFS in toluene-ethylbenzene-cumene series are always larger than those of styrene, see Table 19), in accord with the general picture in vinyl polymerization (see Introduction).

Thermal Copolymerization of PFS and Styrene. Copolymerization of PFS and styrene was carried out in the absence of initiator. The same procedures were followed in evaluating copolymerization parameters. Table 25 gives the data. As expected, the Fineman-Ross treatment yields $r_1 = 0.39 \pm 0.02$ and $r_2 = 0.17 \pm 0.12$ in agreement with those obtained from the AIBN-initiated copolymerization of PFS and styrene. Since ϕ is known to be 7.2 for PFS-styrene copolymerization, the measurement of over-all rates of thermal copolymerization of the same system should permit the detection of any cross-initiation process^{7,44} by using Equation 45. The results are shown in Table 25. Walling⁴⁴ predicted that much larger values of the specific rate of cross-initiation might be expected for more strongly alternating pairs of monomers. The data of Table 25 do not agree with this expectation; the system PFS-styrene, which is appreciably alternating ($r_1 r_2 = 0.093$), the rates observed not only fail to indicate cross-initiation, but are actually lower than those which would be expected from the known rate of thermal polymerization of styrene alone (the thermal rate of polymerization of PFS is slower than that of styrene). There are a few reports available in the literature on cross initiation systems. Walling⁴⁴ studied the thermal copolymerization of styrene and MMA, and found preferential cross initiation, (presumably due to polar effects in the transition state) although the system is only moderately alternating ($r_1 r_2 = 0.26$ ⁵³). Gilbert *et al.*⁸⁰ observed a rapid cross initiation for the vinylidene cyanide-styrene and the

vinylidene-2,5-dichlorostyrene systems. Both of these systems are very strongly alternating ($r_1 r_2 = 5.0 \times 10^{-6}$ for vinylidene cyanide-styrene; 2.8×10^{-4} for vinylidene cyanide-2,5-dichlorostyrene). On the other hand, however, no cross initiation was detected in the case of styrene-diethyl fumarate,⁴³ although the system is strongly alternating also ($r_1 r_2 = 0.021$). Apparently, the generality of such cross initiations is unknown, and the precise interpretation is difficult since the meaning of the value of ϕ in the usual copolymer rate equation is obscure.^{12b}

Thermal Copolymerization of PFS and Methyl Methacrylate.

Copolymerization of PFS and MMA was carried out in the absence of any initiator. Table 27 gives the data. As expected, the Fineman-Ross treatment yields $r_1 = 0.93 \pm 0.11$ and $r_2 = 0.91 \pm 0.25$ (M_2 is PFS), in agreement with those obtained from the AIBN-initiated copolymerization of PFS and MMA. The same procedures were followed in evaluating the specific rate of cross initiation. Table 27 also gives the data. Again, the rates observed indicate no cross initiation.

Copolymerization of PFS and Styrene in Solvents.

PFS and styrene were allowed to copolymerize in a number of solvents. Table 26 gives the results. The Fineman-Ross treatment yields $r_1 = 0.39 \pm 0.01$, $r_2 = 0.30 \pm 0.06$, (M_2 is PFS) for the AIBN-initiated copolymerization of PFS and styrene in benzonitrile; $r_1 = 0.40 \pm 0.02$, $r_2 = 0.56 \pm 0.07$, for the corresponding thermal copolymerization of PFS and styrene in benzonitrile. This result compares with $r_1 = 0.42 \pm 0.01$, $r_2 = 0.22 \pm 0.06$, for the AIBN-initiated and $r_1 = 0.39 \pm 0.02$, $r_2 = 0.17 \pm 0.12$ for the

thermal copolymerization of PFS and styrene in the absence of solvent. Since the rate constant for chain initiation or chain termination does not appear in the copolymerization equation, the equation predicts no dependence of copolymer composition and hence monomer reactivity ratios on the over-all rate of polymerization process, nor upon the particular initiator starting the radical chain. This independence has been confirmed for styrene-MMA radical copolymerization initiated thermally,⁸¹ photochemically,⁸² by benzoyl peroxide,^{16,81-3} by *p*-chlorobenzoyl peroxide,⁸³ by *t*-butyl peroxide,⁸³ by AIBN,⁸⁴ by triisopropylboron,⁸⁵ (a free-radical-type catalyst), by β -ray irradiation,⁸⁶ and by γ -ray irradiation.⁸⁷ With styrene-MMA no change in monomer reactivity ratios has been detected upon the addition of water, ethylbenzene, dodecyl mercaptan, or hydroquinone, or the presence or absence of air,⁸¹ nor by changing the reaction medium from mixtures of pure monomers to monomer solutions in a number of solvents such as ethyl acetate, benzene, or acetonitrile, or even methanol.^{81,82,88,89} However, Bradbury and Melville⁹⁰ studied the copolymerization of styrene and butyl acrylate in benzene solution (using ¹⁴C-labelled AIBN as initiator), and observed an appreciable increase of r_1 and r_2 in the most dilute solution. Drougas and Guile⁹³ also reported a substantial deviation from constant values of r_1 and r_2 in the copolymerization of itaconic anhydride and styrene using benzene and THF as solvents. In recent years, it has been found by several groups of workers⁹¹⁻² that the monomer reactivity ratios of polar vinyl monomers such as acrylonitrile may

be altered by complexing with Lewis acids such as aluminum chloride⁹² and zinc chloride.⁹¹ On the other hand, Overberger *et al.*⁹⁴ observed no difference in monomer reactivity ratios for the copolymer system styrene-*p*-chlorostyrene in solvent mixtures of carbon tetrachloride and nitrobenzene using aluminum bromide, ferric chloride, titanium tetrachloride, stannic chloride and titanium tetrachloride-trichloroacetic acid as catalysts in homogeneous solution. Thus, although the monomer reactivity ratios show general insensitivity to the environment in which polymerization occurs, there are cases where their solvent dependence are not negligible. It is not surprising, therefore, for the present system PFS-styrene to show some positive deviation from constancy of r_1 and r_2 . For example, in benzonitrile solution there is an appreciable increase of r_2 which involves an average increase of PFS content of corresponding polymers of about 8% (compare Tables 25 and 26). It is not known whether this represents a real increase of r_2 or is due to a large amount of transfer to benzonitrile and PFS with consequent incorporation of phenyl groups into the polymer. The latter possibility could be ruled out since the transfer constants to benzonitrile and PFS are approximately zero. Apparently, a systematic study on the monomer reactivity ratios over a wide range of benzonitrile (and on the other solvents as well) concentration would be necessary to completely clarify this observation.

Table 20
Copolymerization of PFS (M_2) and Styrene (M_1) at 60°^a

$[M_1]$	$[M_2]$	Rate $\times 10^5$ ^b	Polymer Composition % M_2 ^c	f	F	ϕ ^d
8.70	0	7.03	0			
7.25	1.22	9.18	23.0	3.35	5.94	10
6.53	1.83	9.54	28.9	2.46	3.56	9.0
5.81	2.44	10.0	32.6	2.07	2.38	7.9
4.36	3.66	11.2	44.7	1.24	1.19	5.6
2.18	5.50	10.4	57.5	0.739	0.396	5.3
1.45	6.11	10.4	65.8	0.520	0.238	4.6
0	7.33	7.66	100			

^aIn the presence of 8.85×10^{-3} M AIBN.

^bIn M sec⁻¹.

^cFrom % carbon in copolymer. Analysis by nmr in carbon tetrachloride was less precise but gave data consistent with these.

^dThe following values were used: M_1 = styrene; M_2 = PFS; $r_1 = 0.42$; $r_2 = 0.22$; $\delta_1^2 = 900$; $\delta_2^2 = 675$; $R_1 = 2k_d f [\text{AIBN}]$, and $k_d = 1.13 \times 10^{-5}$ sec⁻¹. The value of f in pure PFS was determined as 0.52 (see Table 6) and in a 50/50 mixture of styrene and PFS to be 0.55; f in pure styrene is 0.60 (ref.37). In all the calculations in Table 20, f was taken as 0.57. Variation of f between 0.52 and 0.60 does not appreciably affect the value of ϕ .

Table 21

Copolymerization of PFS (M_2) and Methyl Methacrylate (M_1) at 60°^a

$[M_1]$	$[M_2]$	Rate $\times 10^5$	Polymer Composition $\%M_2^b$	f	F	ϕ^c
9.35	0	29.5	0			
7.79	1.22	17.4	14.9			6.0
7.01	1.83	16.4	20.6	3.85	3.83	4.5
6.23	2.44	13.1	27.4	2.65	2.55	5.7
4.68	3.66	11.9	44.8	1.23	1.28	4.6
2.34	5.50	9.92	67.8	0.475	0.425	4.5
1.56	6.11	8.77	79.1	0.264	0.255	6.5
0	7.33	7.66	100			

^aIn the presence of $8.85 \times 10^{-3} M$ AIBN.

^bFrom UV spectroscopy.

^cCalculated using $r_1 = 0.99$; $r_2 = 0.91$; $\delta_1^2 = 46.2$ (ref.38); $\delta_2^2 = 675$; $R_i = 2k_d f [AIBN]$ with $k_d f = (1.13 \times 10^{-5})(0.50) \text{ sec}^{-1}$. The following values of f have been measured: 0.52 in pure PFS; 0.50 in a 50:50 mixture of PFS and MMA; 0.46 in pure MMA (ref.39). The variation of f between 0.52 and 0.46 affects the value of ϕ by less than 8%.

Table 22

Copolymerization Parameters for Several Monomers With Styrene and MMA

M_2	r_1	r_2	$1/r_1$	Q_2	e_2	Temperature, °C
$M_1 = \text{Styrene}$						
Pentachloro- styrene ^{a,b}	1.31	0.35	0.7	0.22	0.52	70°
p-Fluoro- styrene ^c	0.7	0.9	1.4	0.83	-0.12	60°
PFS ^d	0.42	0.22	2.4	0.69	0.74	60°
MMA ^e	0.52	0.46	1.9	0.74	0.40	60°
$M_1 = \text{MMA}$						
Pentachloro- styrene ^{a,b}	4.0	0.35	0.25	0.22	0.52	70°
PFS ^d	0.99	0.91	1.01	0.87	0.75	60°
Styrene ^e	0.46	0.52	2.2	1.00	-0.8	60°

^aSee Young, ref.40.^bSee Alfrey and Ebelke, ref.41.^cSee ref.53 and 75.^dThis study.^eSee Lewis et al., ref.16.

Table 23

A Summary of the Copolymerization Parameters for PFS (M_2)

M_1	r_1	r_2	Q_1	Q_2	e_1	e_2	$k_{12}^{a,c}$	$k_{21}^{b,c}$	ϕ
Styrene	0.42	0.22	1.00	0.69	-0.80	0.74	255(726)	886(2527)	7.2
MMA	0.99	0.91	0.74	0.87	0.40	0.75	254(536)	214(611)	5.3

^a $k_{12} = k_{11}/r_1$, where $k_{11} = 107 \text{ M}^{-1}\text{sec}^{-1}$ for styrene; $251 \text{ M}^{-1}\text{sec}^{-1}$ for MMA (ref.77).

^b $k_{21} = k_{22}/r_2$, where $k_{22} = 195 \text{ M}^{-1}\text{sec}^{-1}$ for PFS.

^cThe values in parentheses were calculated by using k_{11} or k_{22} at 60°C estimated by assuming the following values of the activation energies for propagation: styrene and PFS, 7 kcal/mole (ref.48); MMA, 5 kcal/mole (ref.7d).

Table 24

Values of the Cross-Termination Constant ϕ

System	ϕ	$r_1 r_2$
PFS-styrene ^a	7.2	0.093
PFS-MMA ^a	5.3	0.90
p-Methoxystyrene-styrene ^b	1.0	0.95
p-Methoxystyrene-MMA ^b	24	0.09
Styrene-MMA ^b	14	0.26
Styrene-diethyl fumarate ^c	8	0.028
Styrene-butyl acrylate ^b	150	0.07

^aPresent value.^bSee ref.42.^cSee ref.43.

Table 25
Thermal Copolymerization of PFS (M_2) and Styrene (M_1) at 60^o^a

$[M_1]$	$[M_2]$	Rate $\times 10^5$	Polymer Composition % M_2	f	F	$R_{i,12,th}$ $\times 10^{11b}$	$R_{i,1,th}$ $\times 10^{11c}$	$R_{i,2,th}$ $\times 10^{11d}$	$\frac{R_{i,12,th}}{R_{i,1,th}}$
8.70	0	0.206	0	----	----	----	5.03	----	----
7.25	1.22	0.239	24.0	3.17	5.94	6.30	7.26	14.7	0.868
6.53	1.83	0.257	28.4	2.52	3.57	7.14	8.97	6.54	0.796
5.81	2.44	0.269	35.5	1.82	2.38	7.78	11.3	3.68	0.688
4.36	3.66	0.257	42.2	1.37	1.19	7.29	20.1	1.63	0.363
4.36	3.66	0.251	45.2	1.21	1.19				
1.45	6.11	0.124	70.1	0.427	0.238	2.36	182	0.587	0.013
0	7.33	0.0570	100	----	----	----	----	0.408	----

^aSee footnotes under Table 20. No initiator was added.

^b $R_{i,12,th}$ = rate of "cross-initiation" between monomer 1 and monomer 2 (PFS). $R_{i,12,th}$ is calculated from Equation 45 using $\phi = 7.2$; $r_1 = 0.42$; $r_2 = 0.22$; $\delta_1^2 = 900$; $\delta_2^2 = 675$.

^c $R_{i,1,th}$ is the rate of thermal initiation of monomer 1 calculating from the equation $R_{i,1,th} = \delta_1^2 R_{p,1,th} / [M]^2$ where $\delta_1^2 = 900$ and $R_{p,1,th} = 2.06 \times 10^{-6} M \text{ sec}^{-1}$.

^d $R_{i,2,th}$ is the rate of thermal initiation of monomer 2 (PFS) calculating from the equation $R_{i,2,th} = \delta_2^2 R_{p,2,th} / [M]^2$ where $\delta_2^2 = 675$ and $R_{p,2,th} = 5.70 \times 10^{-7} M \text{ sec}^{-1}$.

Table 26

Thermal Copolymerization of PFS (M_2) and Styrene (M_1) in Solvents, 60°^a

Solvent	[M_1]	[M_2]	Rate $\times 10^6$	Polymer Composition % M_2	f	F
Benzonitrile	4.35	0	0.520	0	----	----
Benzonitrile	3.27	0.916	1.10	32.2	2.11	3.57
Benzonitrile	2.90	1.22	1.25	38.8	1.58	2.38
Benzonitrile	2.18	1.83	2.14	50.3	0.988	1.19
Benzonitrile	2.18	1.83	2.09	51.6	0.938	1.19
Benzonitrile	1.09	2.75	1.22	64.6	0.548	0.396
Benzonitrile	0	3.67	0.427	100	----	----
Benzonitrile ^b	3.63	0.611	44.2	24.3	3.12	5.94
Benzonitrile ^b	3.27	0.916	51.9	31.2	2.21	3.57
Benzonitrile ^b	3.27	0.916	51.2	30.9	2.24	3.57
Benzonitrile ^b	2.90	1.22	66.7	37.1	1.70	2.38
Benzonitrile ^b	2.18	1.83	75.6	44.7	1.24	1.19
Benzonitrile ^b	1.09	2.75	71.2	64.1	0.560	0.396
Benzene	2.18	1.83	0.423	47.0	1.13	1.19
Fluorobenzene	2.18	1.83	0.649	43.9	1.28	1.19
Chlorobenzene	2.18	1.83	0.634	47.7	1.10	1.19
Bromobenzene	2.18	1.83	0.613	46.2	1.16	1.19
Toluene	2.18	1.83	0.633	43.4	1.30	1.19
Benzotrifluoride	2.18	1.83	0.573	48.6	1.06	1.19
Anisole	2.18	1.83	0.803	42.4	1.36	1.19
Anisole	2.18	1.83	0.805	42.0	1.38	1.19
Hexafluorobenzene	2.18	1.83	0.315	50.1	0.996	1.19
MIBK	2.18	1.83	3.57	48.1	1.08	1.19

^aSee footnotes under Table 20. No initiator was added.

^bIn the presence of $[AIBN] = 8.85 \times 10^{-3} M$, and $[PhCN] = 4.90 M$ corresponding to 50% by volume.

Table 27
Thermal Copolymerization of PFS (M_2) and MMA (M_1) at 60°^a

$[M_1]$	$[M_2]$	Rate $\times 10^6$	Polymer Composition % M_2	f	F	$R_{i,12,th}$ $\times 10^{11b}$	$R_{i,1,th}$ $\times 10^{12c}$	$R_{i,2,th}$ $\times 10^{11}$	$\frac{R_{i,12,th}}{R_{i,2,th}}$
9.35	0	0.240	0	----	----	----	0.0304	----	----
7.01	1.83	1.90	21.0	3.76	3.83	1.54	0.0542	6.54	0.235
6.23	2.44	1.01	27.8	2.60	2.55	0.564	0.0686	3.68	0.153
4.68	3.66	0.885	49.0	1.04	1.28	0.624	0.122	1.63	0.383
2.34	5.50	0.632	64.4	0.553	0.425	0.446	0.486	0.772	0.618
1.56	6.11	0.569	78.6	0.272	0.255	0.388	1.09	0.587	0.661
0	7.33	0.570	100	----	----	----	----	0.408	----

^aSee footnotes under Table 21. No initiator was added.

^bCalculated from Equation 45 using $\phi = 5.3$; $r_1 = 0.99$; $r_2 = 0.91$; $\delta_1^2 = 46.2$; $\delta_2^2 = 675$.

^cCalculated from the equation $R_{i,1,th} = \delta_1^2 R_{p,1,th}^2 / [M]^2$ where $\delta_1^2 = 46.2$ and $R_{p,1,th} = 2.4 \times 10^{-7} \text{ M sec}^{-1}$ (Walling, ref.44).

^dCalculated from the equation $R_{i,2,th} = \delta_2^2 R_{p,2,th}^2 / [M]^2$ where $\delta_2^2 = 675$ and $R_{p,2,th} = 5.70 \times 10^{-7} \text{ M sec}^{-1}$.

Figure 20a. Relationship between Copolymer and Feed Compositions.

Curve I: PFS-MMA system ($r_1 = 0.99$, $r_2 = 0.91$), $M_1 = \text{MMA}$.

Curve II: PFS-Styrene system ($r_1 = 0.42$, $r_2 = 0.22$),

$M_2 = \text{PFS}$.

HETEROPOLYMERIZATION

I. EXPERIMENTAL SECTION

Materials. The PFS and AIBN used were purified by the same procedures as those described in the Homopolymerization section. The methanol used in this study was of c.p. grade and was distilled under nitrogen immediately before use.

Kinetics. The polymerization rates were followed by an ampoule technique. Solvent, monomer, and catalyst were added in that order under a stream of nitrogen. The polymer was isolated by the modified freeze-dry technique described in the previous section. The number average molecular weight of the poly-PFS samples was obtained from measurements of intrinsic viscosity in MIBK at 30°, using the Equation 48.

II. RESULTS AND DISCUSSION

Variation of R_p and $\bar{P}$ With $[M]$. The polymerization of PFS in methanol (a diluent that causes precipitation of the polymer) at 60° is homogeneous when the initial monomer concentration is equal to or higher than 2M. However, even under these conditions, the polymerizing system separates in two phases (one dilute and one concentrated in polymer) when a certain conversion is reached. This conversion depends on the solvent-monomer ratio and on the molecular

weight of the produced polymer. For monomer concentrations lower than $2M$, the system becomes heterogeneous from the onset of the reaction. Table 28 shows the data and Figure 21 is a plot of $\log R_p$ vs. $\log [M]$ (where R_p is the observed rate of polymerization in $M \text{ sec}^{-1}$, and $[M]$ is the initial monomer concentration in M) in the presence of a constant concentration of AIBN of $1.85 \times 10^{-4} M$. The figure shows that, as the initial monomer concentration is reduced by the addition of methanol, the rate at first declines, until $[M] \cong 2M$ is reached. Then the rate increases as the monomer concentration diminishes to about $1M$. The rate decreases again when $[M]$ is below $1M$, where the reaction order with respect to monomer is approximately 2 (see the dotted line portion in Figure 21). During the initial decrease in rate the polymer remains in solution, but at the point where the rise in rate occurs the polymer begins to separate as a gelatinous precipitate, and the enhancement of rate is no doubt due to the accompanying reduction in the k_t value. This observation is supported by the concomitant increase in the degree of polymerization as shown in Figure 23. Thus, typical occlusion phenomena⁹⁵ are operative, a reduction in the rate of termination being the dominant feature. In support of this observation, individual runs in this region, *i.e.*, $[M] < 2M$, show a marked autocatalytic effect. As can be seen from Table 28, higher conversion runs always give faster rates under otherwise identical conditions, and consequently the polymerization rate also must be compared at the same conversion. In the region $[M] < 2M$ the rates were determined between 3-5% conversion. However, a few points

determined at conversion somewhat beyond this range do not appear to change the trend of the curve significantly. It should be noted that the polymerization of styrene in methanol has been shown by Abere et al.⁹⁶ to behave like a typical occlusion system also. Chapiro's experiments^{97,98} in initiation by gamma radiation and a more recent study by Odian et al.⁹⁹ on the accelerating effect of methanol on the gamma radiation-induced graft copolymerization of styrene to polyethylene have confirmed this.

Variation of R_p With $[I]$. In order to obtain the variation of the polymerization rate with the initiator concentration under heterogeneous conditions, a series of polymerization experiments with constant initial monomer concentrations (1.83M and 0.611M) and with varying initiator concentrations was carried out. The data are also given in Table 28. Figure 22 shows a double logarithmic plot of the observed rate versus initiator concentration. The reaction order with respect to initiator was found to be 0.8 at $[M] = 1.83M$ and 0.9 at $[M] = 0.611M$. The points at $[M] = 0.611M$ are somewhat scattered probably as a result of a stronger autocatalytic effect. The molecular weight of the polymers prepared at constant concentration of initiator ($1.85 \times 10^{-4}M$) and corresponding to a conversion of about 6%, increases sharply with the monomer concentration changing from about 2M to 1.5M (see Figure 23). The maximum of the molecular weight occurs at a monomer concentration close to that of the maximum rate value. According to Talamini et al.,¹⁰⁰⁻¹ the change of the molecular weight and of the polymerization rate with the initial monomer concentration should follow

the same trend in the absence of a very active chain transfer agent.

An estimation of the chain transfer constant to methanol from the linear portion of a Mayo plot yields a value of 3.55×10^{-5} , which indicates that methanol is not a very active chain transfer agent compared to THF (a very active agent) and supports Talamini's postulate.

Table 28

The Polymerization of PFS in Methanol Initiated by AIBN at 60°C^a

Group Run	[M]	[S]/[M]	[AIBN] $\times 10^4$	Time, hr (at 60°)	Conv'n, %	$R_p \times 10^6$	$[\eta]$	$10^4/\bar{P}$	$[M]^2[I]^{0.9} \times 10^4$
A	7.33	0	1.85			13.0		0.950	
	6.98	0.168	1.85	10	6.49	12.6	----	----	
	6.87	0.225	1.85	10	5.89	11.2	1.76	1.06	
	6.49	0.438	1.85	13	10.7	14.9	1.69	1.12	
	4.89	1.69	1.85	20	5.89	4.00	1.34	1.53	
	3.66	3.37	1.85	7	0.865	1.26	----	----	
	1.83	40.1	1.85	30.3	6.01	1.01	0.88	2.70	
	1.83	10.1	1.85	16.5	1.22	0.377	0.57	4.96	
	1.47	13.5	1.85	20	6.48	1.32	1.84	0.996	
	1.34	15.3	1.85	23	12.0	1.91	----	----	
	0.916	23.6	1.85	2.7	5.29	4.98	1.72	1.09	
	0.733	30.3	1.85	2.8	5.15	3.81	1.56	1.25	2.35
	0.611	37.1	1.85	2.8	3.43	2.11	1.56	1.25	1.63
	0.611	37.1	1.85	5.6	7.76	2.35	----	----	1.63
	0.458	50.6	1.85	2	2.36	1.50	----	----	0.917
	0.407	57.3	1.85	2	2.00	1.13	----	----	0.724

Table 28 (Continued)

Group Run	[M]	[S]/[M]	[AIBN] $\times 10^4$	Time, hr (at 60°)	Convsn, %	$R_p \times 10^6$	$[\eta]$	$10^4/\bar{P}$	$[M]^2[I]^{0.9} \times 10^4$
B	1.83	10.1	0.925	30	7.17	1.22	1.21	1.75	
	1.83	10.1	1.85	16.5	1.22	0.377	0.57	4.96	
	1.83	10.1	3.70	18.5	11.6	3.20	1.35	1.52	
	1.83	10.1	3.70	18	13.5	3.80	-----	-----	
	1.83	10.1	5.55	18.5	22.9	6.30	0.66	4.01	
	1.83	10.1	11.1	10	16.8	8.50	1.28	1.63	

C	0.611	37.1	0.925	6.5	0.901	0.255	0.58	4.78	0.874
	0.611	37.1	0.925	6.5	1.91	0.499	-----	-----	0.874
	0.611	37.1	1.85	5.6	7.76	2.35	1.14	1.90	1.63
	0.611	37.1	1.85	2.8	3.43	2.11	1.56	1.25	1.63
	0.611	37.1	3.70	6.5	1.15	0.301	0.49	6.10	3.04
	0.611	37.1	5.55	3.3	1.21	0.616	0.31	7.35	4.38
	0.611	37.1	5.55	10	12.4	2.10	-----	-----	4.38
	0.611	37.1	11.1	1.5	3.20	3.62	0.44	6.97	8.18
	0.611	37.1	11.1	1.5	3.38	3.82	0.29	7.81	8.18

^a See footnotes under Table 3.

Figure 21. Graph of $\log R_p$ vs. $\log [M]$ for the Polymerization of PFS in Methanol at 60°C . $[\text{AIBN}] = 1.85 \times 10^{-4} \text{ M}$.

Figure 22. Graph of $\log R_p$ vs. $\log [\text{AIBN}]$ for the Polymerization of PFS in Methanol at $[M] = 1.83M$ (●), and at $[M] = 0.611M$ (▲).

Figure 23. Graph of $\bar{P}_n$ vs. $[M]$ for the Polymerization of PFS in Methanol at $[AIBN] = 1.85 \times 10^{-4} M$.

SUMMARY

Homopolymerization

- (1) Thermal polymerization of PFS in bulk was done at different temperatures. The over-all activation energy for thermal polymerization was found to be 16.8 kcal/mole. The number-average degree of polymerization of poly-PFS is higher than that of polystyrene by about 3 times at 60° to about 13 times at 129°. The rates of the polymerization of PFS are similar to those of styrene at the same temperature.
- (2) The polymerization of PFS initiated by AIBN was done at different temperatures. The value of C_M for PFS was found to be zero. The calculated over-all activation energy for the AIBN-initiated polymerization is 20.6 kcal/mole. The values of δ^2 were obtained for pure PFS and PFS-solvent systems.
- (3) The polymerization of PFS initiated by AIBN-³H was done at 60°. It is concluded that the termination mechanism is entirely by combination.
- (4) Thermal polymerization of PFS in solvents was done at 60°. The over-all rates in substituted benzenes are approximately second order in monomer. The transfer constants to solvents were calculated. An extended thermal initiation mechanism of the type proposed by Brown is adopted.
- (5) The measurement of the rate of initiation for PFS was done by

using two different methods: the molecular weight method and the inhibitor method. The molecular weight method gave reasonable values of f for PFS-solvent mixtures. The inhibitor method was less successful. In the cases where DPPH used as inhibitor, abnormal results were obtained. Benzoquinone, however, did give satisfactory data.

- (6) The determination of radical lifetime was done by using the rotating sector method, and the absolute rate constants k_p and k_t are calculated for both pure PFS and the PFS-solvent systems.

Copolymerization

- (1) Copolymerization of PFS and styrene initiated by AIBN was done at 60° . The monomer reactivity ratios, and Q, e values were obtained. The ϕ factor calculated from the kinetic data is 7.2.
- (2) Copolymerization of PFS and MMA initiated by AIBN was done at 60° . The monomer reactivity ratios and Q, e values were obtained. The ϕ factor calculated is 5.3. Based on the chain transfer, the absolute rate constant and the copolymerization data, it is concluded that the PFS monomer is less reactive than styrene, but that the radical is more reactive.
- (3) Thermal copolymerization of PFS and styrene was done at 60° in the absence of initiator. The observed rates fail to indicate cross-initiation. The values of the monomer reactivity ratios were found to be the same as those in the AIBN-initiated copolymerization.

- (4) Thermal copolymerization of PFS and MMA was done at 60° in the absence of initiator. No cross-initiation was observed either. The values of the monomer reactivity ratios were found to be the same as those in the AIBN-initiated copolymerization.
- (5) Copolymerization of PFS and styrene in solvents was done at 60° with and/or without AIBN as initiator. The monomer reactivity ratios are apparently changed in benzonitrile.

Heteropolymerization

The heteropolymerization of PFS in methanol was studied at 60° with AIBN as initiator. It was shown that typical occlusion phenomena are operative in this system.

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APPENDICES

I. A Comparison of the American and the British Conventions in Polymerization Kinetics

(Those expressions which are different in the two conventions
are denoted by the symbol (*))

<u>American Convention</u> ^{7,47}	<u>British Convention</u> ^{55,105-107}
Initiation:	Rate
$I \rightarrow 2R\cdot$	$-d[I]/dt = k_d f[I]$
	$d[R\cdot]/dt = 2k_d f[I]$
$R\cdot + M \rightarrow M\cdot$	$k_i [R\cdot][M]$
Propagation:	Rate
$M\cdot + M \rightarrow M\cdot$	$R_p = k_p [M\cdot][M]$
Termination:	
$M_m\cdot + M_n\cdot \rightarrow M_m - M_n$ (combination)	
	$-d[M\cdot]/dt = 2k_{tc} [M\cdot]^2 (*)$
	$-d[M\cdot]/dt = k_{tc} [M\cdot]^2 (*)$
	$d[P]/dt = k_{tc} [M\cdot]^2 (*)$
	$d[P]/dt = \frac{1}{2}k_{tc} [M\cdot]^2 (*)$
$M_m\cdot + M_n\cdot \rightarrow M_m + M_n$ (disproportionation)	
	$-d[M\cdot]/dt = 2k_{td} [M\cdot]^2 (*)$
	$-d[M\cdot]/dt = k_{td} [M\cdot]^2 (*)$
	$d[P]/dt = 2k_{td} [M\cdot]^2 (*)$
	$d[P]/dt = k_{td} [M\cdot]^2 (*)$
Over-all Rate:	
$R_p = \frac{R_i^{0.5}}{\delta} [M] = \left[\frac{2k_d f}{\delta^2} \right]^{0.5} [M][I]^{0.5}$	$R_p = \frac{R_i^{0.5}}{\delta} [M] = \left[\frac{2k_d f}{\delta^2} \right]^{0.5} [M][I]^{0.5}$
where $\delta = (2k_t)^{0.5}/k_p (*)$ (ref.7b)	where $\delta = k_t^{0.5}/k_p (*)$ (refs.106,107)

The Reciprocal of the Degree of Polymerization:

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_P + C_M + C_S \frac{[S]}{[M]}$$

(combination)

$$\frac{1}{\bar{P}} = \frac{\delta^2}{[M]^2} R_P + C_M + C_S \frac{[S]}{[M]}$$

(disproportionation)

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_P + C_M + C_S \frac{[S]}{[M]}$$

(combination)

$$\frac{1}{\bar{P}} = \frac{\delta^2}{[M]^2} R_P + C_M + C_S \frac{[S]}{[M]}$$

(disproportionation)

The Over-all Rate of Copolymerization:

$$\frac{-d\{[M_1] + [M_2]\}}{dt} = R_P =$$

$$\frac{\{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2\}R_1^{0.5}}{\{r_1^2\delta_1^2[M_1]^2 + 2\delta_1r_1r_2\delta_2[M_1][M_2] + r_2^2\delta_2^2[M_2]^2\}^{0.5}}$$

Same equation

as American

Convention

(refs.106,107)

$$\text{where } \delta_1^2 = 2k_{t11}/k_{11}^2, \delta_2^2 = 2k_{t22}/k_{22}^2 \quad (*)$$

$$\text{where } \delta_1^2 = k_{t11}/k_{11}^2, \delta_2^2 = k_{t22}/k_{22}^2 \quad (*)$$

$$r_1 = k_{11}/k_{12}, r_2 = k_{22}/k_{21}$$

$$r_1 = k_{11}/k_{12}, r_2 = k_{22}/k_{21}$$

$$\phi = \frac{k_{t12}}{2(k_{t11} k_{t22})^{0.5}} \quad (*)$$

$$\phi = \frac{k_{t12}}{(k_{t11} k_{t22})^{0.5}} \quad (*)$$

If all collisions are equally effective

If all collisions are equally effective

$$\phi = 1 \text{ (refs.7c,47b)}$$

$$\phi = 1 \text{ (refs.42,106,107)}$$

Thus the equations derived with the American Convention or the British Convention may be readily interchanged by the following relationships:^{12c}

$$2k_{tc} \text{ (American)} \equiv k_{tc} \text{ (British)}$$

$$2k_{td} \text{ (American)} \equiv k_{td} \text{ (British)}$$

Note that δ^2 has same numerical value in the two conventions.

II. Some Remarks About the Rotating Sector Technique

The Set-up. The following schematic diagram shows the set-up used in this study:

Notations from left to right:

- S: The light source is a 100-watt General Electric Ultraviolet Mercury lamp supplied with power system (E.H. Sargent & Co. Catalog No. S-44260). The power system should be kept in a basket containing Dry-Ice to reduce the heat produced by the system. The lamp could be kept cooling by a regular blower.
- I₁: An iris with a circle opening ca.4 cm in diameter. The portion close to the light source is made of aluminum foil.
- D: The sector disc with adjustable opening made by Bausch & Lomb Optical Co., Rochester, N.Y. The motor used, Bodine model 805SBK46, was made by Bodine Electric Co., Chicago, Ill. The

speed reducer APCOR model No.2401 was made by Geartronics Corporation, North Billerica, Mass. The disc, the motor and the speed reducer were all mounted on the same heavy steel plate to insure the reproducibility of the disc rotation.

I_2 : An iris with adjustable opening. (ca. 4 cm in diameter was used in this study).

F: A filter, Corning C. S. 0-52, made by Corning Glass Works, Parkersburg, W. Va. This filter was fixed on I_2 .

I_3 : An iris with circle opening ca. 4 cm in diameter.

L_1, L_2 : Glass lenses supplied by Edmund Scientific Co., Barrington, N.J. 08007. All are $3\frac{1}{2}$ inch in diameters. L28X

L_3 : A Mercury reading glass lens, 3 inch in diameter.

I_4 : An iris with adjustable circle opening. An opening with ca. 4 cm in diameter was used in this study.

T: A thermostat bath, wrapped with aluminum foil (or kept in a box).

R: A reaction cell.

OB: An aluminum bench of 1 meter long (Ealing Corporation, Cambridge, Mass. catalog No. 22-681).

Note that I_2 , F, L_1 , L_2 , L_3 , I_4 were all fixed on OB. All parts in this set-up should be fixed including the source S, the cell R, etc.

This is important for obtaining the reproducible rates.

A Sample Calculation of Average Radical Lifetime. The dark rate of polymerization for PFS is $0.11 \times 10^{-6} \text{ M sec}^{-1}$ at $[\text{ACHN}] = 3.00 \times 10^{-3} \text{ M}$. The corresponding rate under steady light is $5.50 \times 10^{-6} \text{ M sec}^{-1}$ (see Table 15). Therefore, the thermal correction factor,

$z = \text{dark rate/steady light rate} = 0.02$. The differences between the theoretical and experimental curves (for $z = 0.02$ and $r = 2$) as measured from Figure 20 are as follows for pure PFS:

$\frac{R_p}{R_{Ps}}$	<u>Difference (= $\log \tau$)</u>
0.565	0.29
0.519	0.26
0.465	0.24
0.428	0.26

Average $\log \tau = 0.263$, $\tau = 1.83$ sec. Note that in all experiments in Table 15, the points lying near midway between the limits of the theoretical curve were chosen for the calculation of the average lifetime. The accuracies were 5-20%. By measuring the lifetime at various rates of polymerization, the accuracy of the determination of the rate constants could be improved.¹⁰ A plot of rate against reciprocal lifetime will give a straight line from the slope of which the ratio $2k_t/k_p$ can be computed (see Equation 22).

III. THE KINETICS OF DIRADICAL POLYMERIZATION

The Over-all Rate and the Activation Energies. The bimolecular diradical mechanism proposed by Flory^{57a} for the thermal polymerization of styrene is as follows:

If the rate of termination is assumed to be bimolecular as in the case of monoradical-initiated polymerization, then it follows from the steady state condition $R_i = R_t$ that $k_i[M]^2 = 2k_{bt}[\cdot M]^2$ and the rate of polymerization is then given by

$$R_p = k_p[\cdot M][M] = k_p(k_i/2k_{bt})^{1/2}[M]^2 \quad (iv)$$

This mechanism leads to a second-order rate for thermal polymerization of PFS in agreement with experiment. If, on the other hand, the termination is a first-order process (e.g., intramolecular coupling), step (iii) will be replaced by step (v):

At steady state $k_i[M]^2 = k_{ct}[\cdot M]$, and the rate of polymerization is given by

$$R_p = k_p[\cdot M][M] = k_p k_i / k_{ct} [M]^3 \quad (vi)$$

Thus a first-order termination process would raise the over-all order for the polymerization to 3. If the termination is entirely by transfer reaction, the step (iii) will be replaced by step (vii):

At steady state $k_i [M]^2 = k_{tr, M} [\cdot M] [M]$ and the over-all rate of polymerization is given by

$$R_p = k_p [\cdot M] [M] = k_p k_i / k_{tr, M} [M]^2 \quad (\text{viii})$$

Thus the over-all rate is second order in monomer also. However, the activation energy equation derived from Equation (viii) will be

$E_{th} = E_p + E_{i, th} - E_{tr, M}$ which is different from $E_{th} = E_p + (E_{i, th} - E_{bt})/2$ derived from Equation (iv). The actual termination mechanism for the thermal polymerization of PFS may be a combination of Equations (iii) and (vii) instead of the combination of (iii) and (v) so that the over-all rate may be second order in PFS in agreement with experiment.

The Relationship Between the Over-all Rate and the Degree of Polymerization. In the presence of solvent, the following step may be added:

It follows from Equations (i) - (iii), (vii) and (ix) that the degree

of polymerization may be given by

$$\bar{P} = \frac{-d[M]/dt}{d[P]/dt} = \frac{k_p [\cdot M \cdot] [M]}{k_{bt} [\cdot M \cdot]^2 + k_{tr,M} [\cdot M \cdot] [M] + k_{tr,S} [\cdot M \cdot] [S]}$$

or

$$\frac{1}{\bar{P}} = \frac{k_{bt}}{k_p [M]} \left(\frac{R_i}{2k_{bt}} \right)^{\frac{1}{2}} + C_M + C_S \frac{[S]}{[M]}$$

where $C_M = k_{tr,M}/k_p$, $C_S = k_{tr,S}/k_p$

Since $R_p = k_p [M] (R_i/2k_{bt})^{\frac{1}{2}}$ and assuming $\delta^2 = 2k_{bt}/k_p^2$,

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2[M]^2} R_p + C_M + C_S \frac{[S]}{[M]} \quad (x)$$

Thus the relationship between R_p and $\bar{P}$ for Flory diradical polymerization is the same as that of monoradical-initiated polymerization (see Equation 13).

VITA

Tzu-Lee Huang was born in Tsingkiang, Fukien, China on October 12, 1938. He was educated in Tze-Yang Elementary School in Tsingkiang and Ta-Tung Public School in Taichung, Taiwan. He was admitted to Provincial First Middle School in Taichung in September of 1949 and graduated in July of 1956. He entered Provincial Chung-Hsing University in July of 1956 and received the Bachelor of Science degree in July of 1960. He was commissioned as a second lieutenant in The Chinese Army and completed his military service in October of 1961. After a short period teaching in the Taichung Middle School system, he returned to Chung-Hsing University as an assistant instructor of chemistry in March of 1962.

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EXAMINATION AND THESIS REPORT

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Title of Thesis: The Kinetics of Polymerization of Pentafluorostyrene

Approved:

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EXAMINING COMMITTEE:

Date of Examination:

March 18, 1970