Radical Production from the Interaction of Closed-Shell Molecules. 4. 1,4-Diradicals and the Isotope Effects on the Spontaneous Polymerization of Pentafluorostyrene[1-3]

William A. Pryor,* Masashi Iino, and George R. Newkome

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

Received January 24, 1977

Abstract: Kinetic isotope effects are reported for the spontaneous "thermal" (i.e., self-initiated) polymerization of 2,3,4,5,6-pentafluorostyrene-β,β-d_2. The isotope effect at 130 °C is about 0.9_7. This is similar to the value reported for styrene.[4] Therefore, the polymerization of pentafluorostyrene (PFS), like styrene, does not involve eq 4 as an important process for converting diradicals to monoradicals. Nevertheless, it is argued that the spontaneous polymerization of PFS involves initiation by diradicals, and data on the scavengers galvinoxyl and 1,3-bis(diphenylene)-2-phenylallyl (BDPA) are presented to prove this. In contrast with the data for styrene, both these scavengers disappear in PFS at 100 °C in reactions that have virtually the same rate constant and are first order in scavenger. Transfer data on toluene and diphenylmethane with PFS agree with our earlier data[9] and show that added transfer agents produce a dramatic increase in the rate of polymerization of PFS. We infer from this that the most important mechanism by which diradicals are converted to monoradicals is by chain transfer to materials, either endogenous or added, that have benzylic hydrogens. The endogenous compounds that have benzylic hydrogens include all cyclic oligomers (such as diarylcyclobutanes) and polymer.

Reactions in which closed-shell molecules interact to produce free radicals can be envisioned as belonging to three mechanistic classes: molecule-assisted homolyses (MAH), one-electron transfer,[2,3] and nonconcerted pericyclic reactions. The work described here was begun in the hope of demonstrating the trapping of 1,4-diradicals produced from 2 + 2 cycloaddition reactions using the techniques of polymer chemistry. Specifically, we have studied the spontaneous ("thermal") polymerization of styrene-like monomers; it seemed likely that some of these monomers form 1,4-diradicals which are able to initiate polymerization in competition with closure to cyclobutane derivatives.[4-6]

The most widely accepted mechanism[1,4,7-10] for the production of radicals in styrene itself is shown in Figure 1A. It postulates the formation of a Diels-Alder adduct, AH, between two styrene molecules (reaction a in Figure 1) and a molecule-assisted homolysis[1,11] reaction of AH with a third styrene molecule (eq c). Although this mechanism has received support from experiments reported by many laboratories, most of the evidence is, at best, consistent with it.[4] The data demonstrate the *presence* of AH, but the reality of the MAH reaction, eq c, has received little direct confirmation.

Furthermore, it appears clear that a single mechanism cannot rationalize the thermal polymerization of all monomers. For example, it is difficult to explain the spontaneous polymerization of methyl methacrylate (MMA)[5] or of 2,3,4,5,6-pentafluorostyrene[9] (PFS) by a mechanism involving a Diels-Alder adduct. Even styrene-like monomers must form radicals by more than one mechanism. For example, the ratios of moles of polymer/dimer/trimer formed from 100 g of styrene (at 85 °C, in units of micromoles) are 15:75:800; whereas for 2-vinylthiophene these data (100 °C, μmol/100 g monomer) are $20{:}4 \times 10^4{:}0$.

Figure 1 outlines the reactions of a styrene-like monomer. In this scheme, monomers are envisioned as reacting to form either a Diels-Alder dimer similar to AH (eq a) or a 1,4-diradical (eq b); some monomers may do both. The Diels-Alder adduct AH can undergo: MAH reaction with monomer to form radicals (eq c); bond scission to form a 1,4-diradical (eq e), or an ene reaction with monomer to form a trimer of the A-Sty type (eq f).[4] Figure 1A also shows possible reactions of the pair of radicals, A· and HM·, produced from the MAH reaction of AH. The radical pair can: diffuse apart and initiate polymerization (eq g); undergo a combination reaction to form trimer of the A-Sty type (eq h); or undergo disproportionation yielding the phenyltetralin-type products that are observed (eq i).

The 1,4-diradical ($\cdot M_2 \cdot$ in Figure 1) could react by: undergoing growth at both ends, i.e., growing as a diradical (eq n); undergoing ring closure to form a cyclic oligomer (eq j); or undergoing transfer to convert it to monoradicals (eq k-m). The oligomeric diradical $\cdot M_n \cdot$ also partitions between growth, cyclization (eq r), and transfer (eq q).

It is difficult to conceive of any mechanism other than some variant of a 1,4-diradical mechanism that is applicable to PFS and MMA. Furthermore, even styrene itself may undergo polymerization via the 1,4-diradical pathway to a small extent.[4,7] However, the nature of the polymer in all these systems suggests that most of it grows as a normal monoradical.[4] Thus, the pathway for conversion of diradicals to monoradicals is central to any mechanism involving 1,4-diradicals, and it is this problem that is the subject of this report.

The earliest mechanism for the conversion of diradicals to monoradicals was suggested by Flory in 1937 to explain the polymerization of styrene.[12] This mechanism, shown in eq 1 and 2 ($Ar = C_6H_5$)

$$2ArCH{=}CH_2 \rightarrow Ar\dot{C}HCH_2CH_2\dot{C}HAr \qquad (1)$$

$$(\cdot M_2 \cdot)$$

$$(\cdot M_2 \cdot) + ArCH{=}CH_2 \rightarrow ArCH{=}CHCH_2\dot{C}HAr + Ar\dot{C}HCH_3 \qquad (2)$$

involves the transfer of a β-hydrogen atom from the 1,4-diradical to a third styrene molecule. It was to test this mechanism that data[4] on the polymerization of styrene-β,β-d_2 were reported by Hammond and Kopecky, Kopecky and Evani, and our own laboratory.[13] These isotope effect data demonstrate that eq 3 and 4 ($Ar = C_6H_5-$) cannot be a predominant source of radical production in styrene.[13]

$$2ArCH{=}CD_2 \rightarrow Ar\dot{C}HCD_2CD_2\dot{C}HAr \qquad (3)$$

$$Ar\dot{C}HCD_2CD_2\dot{C}HAr + ArCH{=}CD_2 \rightarrow ArCH{=}CDCH_2\dot{C}DAr + Ar\dot{C}HCD_3 \qquad (4)$$

In this context, pentafluorostyrene is particularly intriguing. It undergoes thermal polymerization at a rate which, although

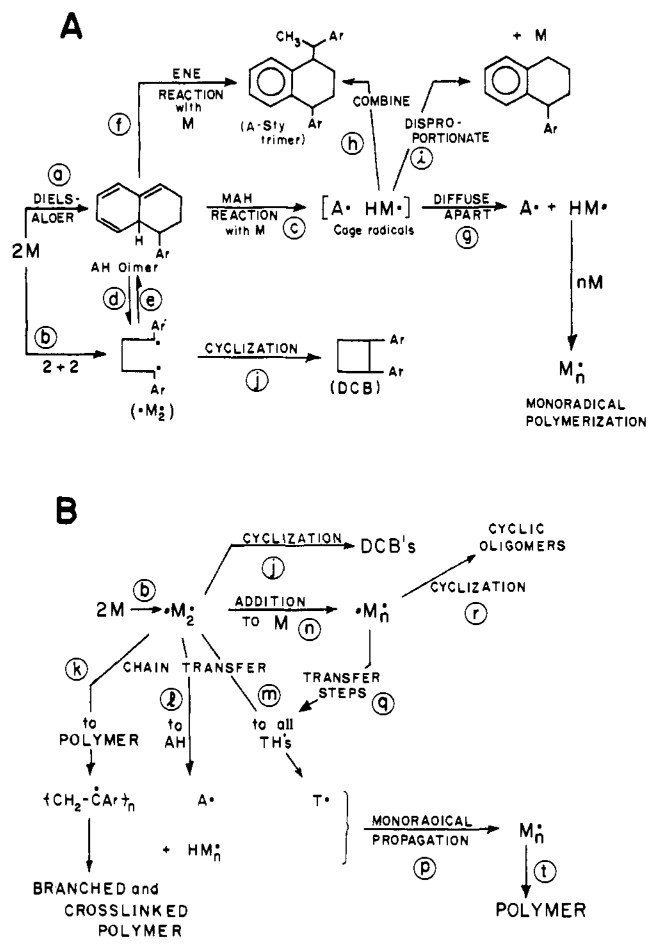


Figure 1. A generalized mechanism for production of the Diels-Alder adduct AH and the 1,4-diradical $\cdot M_2\cdot$ from styrene-like monomers. The possible subsequent reactions of AH are shown. Also shown are possible mechanisms by which diradicals may be converted to monoradicals. This figure is modified and expanded from a similar one presented in ref 4.

slower than that of styrene, is still quite appreciable.[4d,9] In the belief that PFS is a particularly likely candidate for 1,4-diradical polymerization,[14] we have measured the kinetic isotope effects on the thermal polymerization of PFS-β,β-d_2, eq 3-4 (Ar = C_6F_5-). As will be seen, the isotope effects are not in accord with eq 4 being an important pathway for the conversion of diradicals to monoradicals for PFS. However, we continue to feel that PFS undergoes thermal polymerization by a diradical initiation mechanism, and we here present transfer and scavenger studies which lend some credence to that postulate.

Experimental Section

Synthesis and Purification of PFS-β,β-d_2. The deuterated olefin was prepared from iodomethane-d_3 (>99% d_3) by the route shown in eq 5-7. Protium material was prepared in the same way, purified by the same methods, and polymerized as a control to obtain k_H values. The preparation of PFS-d_2 in acceptable purity proved to be an extremely difficult task; the acetate could be cracked (eq 7) only at high temperatures, and the PFS-d_2 required careful preparative GLC, with considerable loss in yield, for satisfactory purity to be obtained.[15,16] Numerous other methods of dehydration were examined, but none gave better results.

$$CD_3MgI + C_6F_5CHO \xrightarrow{85\%} \underset{\mathbf{1}}{C_6F_5C(OH)HCD_3} \qquad (5)$$

$$\mathbf{1} + Ac_2O \underset{90\%}{\xrightarrow{\text{pyridine}}} \underset{\mathbf{2}}{C_6F_5C(OAc)HCD_3} \qquad (6)$$

$$\mathbf{2} \underset{60\%}{\xrightarrow{\text{hot tube}}} \underset{\text{PFS-}d_2}{C_6F_5CH{=}CD_2} \qquad (7)$$

A. **α-Pentafluorophenylethanol-β,β,β-d_3 (1).** Typical results from several runs were as follows. To methylmagnesium iodide (prepared by a standard procedure from magnesium (3.0 g, 0.12 mol) and iodomethane-d_3 (11.8 g, 0.081 mol, N.E.N. Co.) in 30 mL of anhydrous ether was added a solution of pentafluorobenzaldehyde (18 g, 0.092 mol; Penisular Chemical Co.) in 30 mL of ether at 0 °C, followed by refluxing for 24 h. Distillation (60 °C, 1.0 mm) yielded 15 g (86%) of **1**.

B. **Acetate 2.** This alcohol was acylated with 5 mol % excess acetic anhydride in five times its volume of dry pyridine, at 0 °C. Washing and extraction gave acetate in 90% yield; bp 69-70 °C (2.4 mm); NMR showed peaks at δ 2.08 (singlet) and δ 6.05 (singlet) for the acetate methyl and α-H and indicated essentially 100% deuteration at the β position.

C. **Pyrolysis of Acetate.** The acetate plus 0.1% *p-tert*-butylcatechol w/w were pyrolyzed by dropping (ca. 15 drops/min) the mixture down a 40 × 2 cm tube filled with glass helices and heated to 600 °C and trapping the effluent in a trap cooled to −20 °C.[15] The product was 98% pure by GLC and was distilled through a spinning band column (bp 62 °C (50 mm)) followed by preparative GLC at 80 °C using 15-30-μL aliquots and a ½-in. column with 10% Bentone 34-DIDP on Chromosorb P 60/80. The material appeared to be 99.41% pure by analytical GLC after distillation and 99.9+% pure after preparative GLC.

Polymerization Method. From 0.5 to 2.3 g of PFS or PFS-d_2 was sealed into an apparatus at about 10^{-6} mmHg; the apparatus contained two (or more) ampules connected by a distillation column and appropriate break seals for attaching to a vacuum line. Monomer was vacuum transferred into the first ampule, the apparatus sealed from the vacuum line, and then monomer was distilled from the first ampule to the second, which was sealed off. The rates of polymerization were measured in this ampule, which was held in a constant temperature bath at 130 °C on a shaker arm so the ampule could be agitated during the entire polymerization. (A series of preliminary runs showed that shaking improved reproducibility.) After reaction, the ampule was again connected to the vacuum line and unreacted monomer was pumped off at 0 °C. The polymer was dissolved in a small amount of methyl isobutyl ketone, precipitated with methanol, filtered, dried, and weighed. If, as was common, the polymer would not entirely dissolve, then the entire methanol fraction was used to isolate the polymer by vacuum drying on the high vacuum line. The ampules were protected from room light throughout the entire sequence.

Scavengers. Galvinoxyl, prepared by Hendrickson[2,3] by the method of Bartlett and Funahashi,[17,18] was used without further purification. Kolesch's radical, 1,3-bis(diphenylene)-2-phenylallyl (BDPA), prepared by the method of Kuhn and Neugebauer,[19] was recrystallized from benzene and dried in a vacuum oven at 100 °C for 5 days to give material with ultraviolet maximum (in benzene) at 489 nm and ϵ 2.87 × 10^4.

The kinetics of scavenger decolorization in styrene or PFS were followed by sealing a weighed amount of the scavenger into a UV cuvette on a glass arm and vacuum transferring in monomer on a high vacuum line; the solution was then freeze-thawed several times and the ampule sealed. In general, the monomer that was used was vacuum transferred into the UV cuvette from another ampule in which it had been heated in an oil bath and allowed to undergo a prepolymerization step to about 10% conversion.

Results

Kinetic Isotope Effect Data. Table I shows data in which comparably prepared protium and deuterium PFS were polymerized at 130 °C. The data are disappointingly irreproducible. We ascribe this to impurities in the PFS which appear to be produced in the high temperatures necessary to crack the PFS acetate and not removed by preparative GLC. Despite the lack of reproducibility, it is clear that a primary kinetic isotope effect is not involved in the polymerization of PFS-β,β-d_2; therefore, eq 4 cannot be an important step controlling the conversion of diradicals to monoradicals.

Data on Transfer by Molecules with Benzylic Hydrogens. Table II presents data which supplement those we previously reported[9] measuring the effect of transfer agents on the polymerization of PFS. Most of these runs were done using 2 g of commercial PFS which had been purified by distillation and

Table I. Polymerizations of Neat Synthetic PFS and PFS-$\beta,\beta,$-d_2 at 130 °C

Monomer	Time, h	% conversion	Rate, %/h
PFS	7.00	4.08	0.58
PFS	6.35	3.29	0.52
PFS	6.33	3.67	0.58
			k_H av 0.56 ± 0.035
PFS-d_2	7.00	3.52	0.50
PFS-d_2	7.00	4.39	0.63
PFS-d_2	5.00	3.10	0.61
PFS-d_2	5.00	2.90	0.58
			k_D av 0.58 ± 0.057

column chromatography through an alumina column (Woelm W 200 basic) just before use.

Experiments with Scavengers. In an effort to shed further light on the initiation mechanism of PFS and to probe the differences between PFS and styrene, experiments were performed in which the rates of decolorization of scavengers were followed. We examined the reactions of two scavengers with PFS and styrene: galvinoxyl and 1,3-bis(diphenylene)-2-phenylallyl (BDPA).

Styrene. The reaction of a number of scavengers with styrene have been reported and the data have been reviewed.[4g] All the scavengers studied to date, including DPPH, benzoquinone, sulfur, oxygen, and iodine, disappear much faster than radicals would be formed from eq 8-9. This has been explained as due either (or both) to reaction of the scavengers with AH or by direct addition of the scavengers to styrene.[4g] In agreement with this, we found that the reaction of styrene with galvinoxyl at 100 °C follows zero-order kinetics, as expected if the scavenger undergoes reaction with AH (or with A· and HM·) as fast as they are formed (eq 8-10). As expected, galvinoxyl disappears faster than the rate at which radicals would be formed from eq 8-9.

However, BDPA, which also disappears with zero-order kinetics, appears to be the first scavenger yet discovered which reacts only with radicals produced from styrene by eq 8-9 and not with styrene itself or AH. The rate of the disappearance of BDPA in styrene at 100 °C, $-d(\text{BDPA})/dt$, is 1.6×10^{-8} mol L^{-1} s^{-1} and is, within experimental error, equal to the rate at which radicals are formed as calculated from the rate of thermal initiation of thermal polymerization,[20] $R_{i,\text{th}} \simeq 1.3 \times 10^{-8}$ mol L^{-1} s^{-1}.

$$2\text{M} \rightleftharpoons \text{AH} \qquad (8)$$

$$\text{AH} + \text{M} \xrightarrow{\text{slow}} \text{A}\cdot + \text{HM}\cdot \qquad (9)$$

$$\text{A}\cdot\ (\text{or HM}\cdot) + \text{scav} \xrightarrow{\text{fast}} \text{decolorized products} \qquad (10)$$

Pentafluorostyrene. The reaction of galvinoxyl and BDPA with PFS was also studied at 100 °C and proved to be even more novel and informative than the comparable data for styrene. In contrast with the situation for styrene, both inhibitors disappear at the same rate in PFS (see Table III). However, rather than disappearing in a zero-order reaction, as expected if radical production were rate limiting (eq 8-9), the disappearance of both scavengers follows a first order rate plot to better than 90% reaction. (Typical data are shown in Figure 2.) These unexpected data can be rationalized in one of two ways. Both scavengers could be postulated to react directly with PFS in an addition reaction. We do not favor this explanation, since it would have to be postulated that both scavengers add to PFS with the same rate constant, and this appears rather unlikely in view of the differing polar character of galvinoxyl and BDPA and the expected importance of polar factors in the reaction of an olefin like PFS. Alternatively, it could be postulated that 1,4-diradicals are produced in a rapid, reversible equilibrium and that the scavengers react in a rate limiting step with $\cdot\text{M}_2\cdot$ or $\cdot\text{M}_n\cdot$.

$$2\text{M} \rightleftharpoons \cdot\text{M}_2\cdot \overset{(n-2)\text{M}}{\rightleftharpoons} \cdot\text{M}_n\cdot \qquad (11)$$

$$\cdot\text{M}_2\cdot\ (\text{or } \cdot\text{M}_n\cdot) + \text{scav} \xrightarrow[\text{limiting}]{\text{rate}} \text{decolorized products} \qquad (12)$$

Discussion

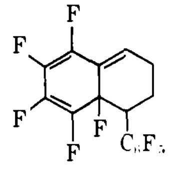
The data in Table I show that the kinetic isotope effect on the thermal polymerization of PFS-β,β-d_2 is $k_H/k_D \simeq 0.9_7$. (Styrene, for comparison, gives about 0.88.[13]) These data clearly do not allow eq 4 to be a major process controlling the rate of conversion of diradicals to monoradicals.[4,21]

In retrospect, it is perhaps unlikely that a process like eq 3-4 could be important for either styrene or PFS. For styrene, as we have pointed out before,[4e] the 1,4-diradical would be expected to abstract a hydrogen atom from AH, the most active hydrogen donor present

$$\cdot\text{M}_2\cdot + \text{AH} \rightarrow \text{HM}_2\cdot + \text{A}\cdot \qquad (13)$$

rather than donating a hydrogen atom to another styrene molecule as in eq 4. (The transfer constant of AH, is at least 1.[1,4,8])

For PFS, it is likely that A′F, the analogue of AH, is produced in only low yield if at all. If A′F is formed, it must be quite unreactive, in contrast to the extraordinarily high reactivity of the styrene's AH. The observed chain transfer constant of bulk PFS, which must include contributions to transfer from any A′F which is present, eq 14, is very near zero.[9] If A′F does



(A′F)

$$+ \text{M}_n\cdot \longrightarrow \text{A}'\cdot + \text{M}_n\text{–F} \qquad (14)$$

Table II. Rates of Polymerization of PFS and Styrene in the Presence of Transfer Agents with Benzylic Hydrogens

Monomer	Temp, °C	Additive	Wt %	Time, h	% conversion	Rate. %/h
PFS	100	None		15.7	2.64	0.17
PFS	100	Toluene	8.3	15.7	3.84	0.24
PFS	100	Toluene	8.4	13.1	3.60	0.28
PFS	100	Diphenylmethane	9.6	13.1	5.82	0.44
Styrene	60	None		19.7	1.99	0.10
Styrene	60	Benzene	42.9	53.0	2.71	0.051
Styrene	60	Toluene	46.6	96.0	4.51	0.047
Styrene	60	Toluene	42.6	50.7	2.34	0.046
Styrene	60	Diphenylmethane	46.1	22.95	1.37	0.060

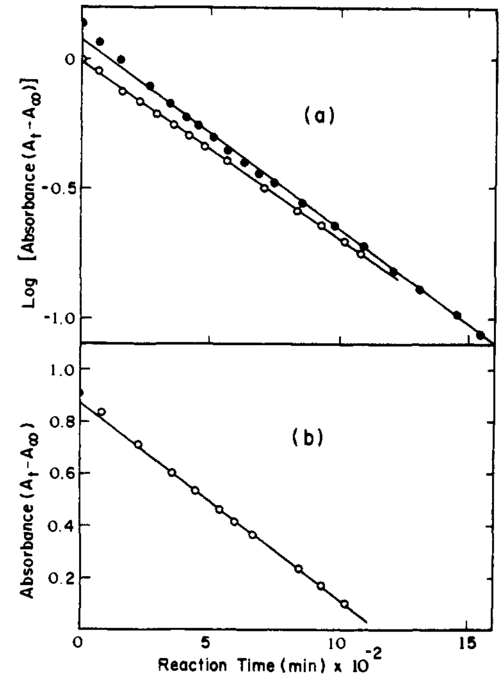
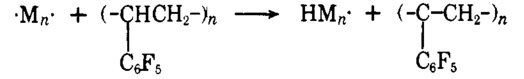


Figure 2. Plots of the decoloration of scavengers in olefins at 100 °C: (a) first-order plots for the decay of 1,3-bis(diphenylene)-2-phenylallyl (BDPA), ○, and galvinoxyl, ●, in PFS: (b) zero-order plot for the decay of BDPA in styrene.

not react with radicals (eq 14), it certainly would not be expected to donate a fluorine atom to an olefin molecule.

Monoradical Production by Transfer. We suggest that a more likely mechanism than eq 3-4 for the conversion of diradicals to monoradicals for PFS involves transfer to materials formed in situ that have benzylic hydrogens. Possible transfer agents include all dimeric and trimeric oligomers shown in Figure 1 as well as the PFS polymer. That is, the conversion of diradicals to monoradicals in the PFS thermal initiation could involve processes like eq 15 or 16. Our first hint that eq 15 might be an important process came from a recognition that PFS undergoes a polymer cross-linking process in thermal polymerizations even at very low conversions.[4h] In neat polymerizations, the PFS polymer appears to be cross-linked even at conversions as low as 1%.[22] Thus, in contrast to styrene, where transfer to polymer can be neglected until relatively high concentrations of polymer are present, PFS appears to undergo transfer to polymer very early in the polymerization.



$$\cdot M_n\cdot + (\text{-}\underset{C_6F_5}{\underset{|}{C}}HCH_2\text{-})_n \longrightarrow HM_n\cdot + (\text{-}\underset{C_6F_5}{\underset{|}{\dot{C}}}\text{-}CH_2\text{-})_n \qquad (15)$$

(16)

If transfer to polymer and to cyclobutane-type dimers is important, and if this step converts diradicals to the more efficiently propagating monoradicals, then transfer agents, TH, with benzylic hydrogens should lead to an accelerated rate of production of polymer from PFS. Although acceleration of polymerization by transfer agents is not unknown, styrene itself appears to undergo transfer to materials like toluene by the classical Flory-Mayo mechanism without complication and with no rate effect other than that produced by dilution of monomer by the nonpolymerizing transfer agent.[4,11] Although this appears to be well accepted in the literature,[4i] we performed a few experiments to demonstrate it. The data in Table II show that transfer agents such as toluene and diphenylmethane, even when present in very high concentrations, affect the rate of polymerization of styrene only by the influence they have on the concentration of monomer.[4,11]

Table III. Rate Constants for the Disappearance of Galvinoxyl and BDPA in Styrene or PFS at 100 °C

	Scavenger		
Olefin	Name	Kinetic order	k
Styrene	Galvinoxyl	Zero	3×10^{-5} [b]
Styrene	BDPA	Zero	1.60×10^{-8} [b]
PFS	Galvinoxyl	First	2.6×10^{-5} [a]
PFS	BDPA	First	2.8×10^{-5} [a]

[a] $-d(\text{scav})/dt = k(\text{scav})$; units of k are L mol^{-1} s^{-1}. [b] $-d(\text{scav})/dt = kt$; units of k are s^{-1}.

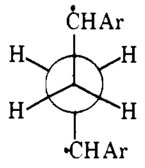
In marked contrast to styrene, our previously reported transfer data on PFS appear to demonstrate that the rate of polymerization of this monomer is greatly increased by added transfer agents.[23] However, we wished to repeat these experiments for several reasons. Firstly, our earlier data employed relatively high concentrations of transfer agents like toluene, and a co-solvent (THF) had to be used because of the insolubility of the transfer agents in neat PFS. Secondly, the older PFS was less pure then our present material.[22] And, thirdly, we wished to obtain data with transfer agents TH at low concentrations that might be reasonable models for the total transfer activity that the cyclic oligomers plus polymer might provide in thermal polymerizations of neat PFS.

Table II shows data of this sort. Transfer studies were done using toluene and diphenylmethane as models of TH. Concentrations of about 8% were used as a compromise between the still lower values we would have liked to use and values which we felt would produce easily measureable rate effects. As the data of Table II show, PFS undergoes a very dramatic increase in its rate of polymerization upon addition of TH-like transfer agents.

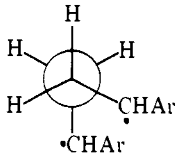
Some Predictions and Some Problems. The Diels-Alder AH mechanism for styrene predicts that the rate of polymerization should be zero initially and should reach a steady-state value when the concentration of AH reaches its steady state. This apparently occurs at low conversions that cannot be conveniently studied, and this prediction has not been confirmed. (However, the sum of the transfer activity of all transfer agents is lower at very low conversions than is true later when AH has reached its steady-state level.[4j]) In a similar way, the diradical-transfer mechanism suggested here predicts that the rate of polymerization should be zero until the concentrations of transfer agents begin to build up. We have not attempted to test this prediction, since it probably is not possible to study the low conversions necessary in the PFS system if they cannot be studied for styrene.

Since DCB's and polymer increase in concentration with conversion, rather than reaching a steady-state level as does AH, the diradical-transfer mechanism predicts that the rate of polymerization should not be constant, but rather should increase with conversion. Our data do not reflect this. However, it is possible that changes in the rate of polymerization caused by precipitation of polymer offset the effects of increasing concentrations of the transfer agents. The polymerization of PFS reaches higher viscosities at low conversions relative to styrene, and this also may affect R_P in a way to oppose the effects of increasing concentrations of transfer agents.

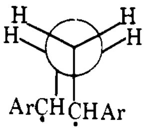
The diradical-transfer mechanism also requires that reaction of the 1,4-diradical with transfer agents competes with its cyclization to cyclobutanes. Indeed, this is a fundamental problem of any mechanism involving 1,4-diradicals, and it is the one that most critics have focused on; we have suggested possible answers to some of the objections in our review.[4k] In the particular case of PFS, it seems clear that conformational equilibration among different rotomers of the 1,4-diradical is faster than is closure to DCB's.[14e] If we assume that some fraction of the 1,4-diradicals are formed in the trans-like conformation **3** that cannot undergo ring closure, and that



3



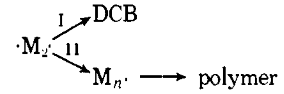
4



5

rotomers **4** and **5** undergo ring closure with zero activation energy, then the apparent activation energy for ring closure is equal to the energy that converts conformer **3** to **4** or **5**. (These assumptions appear reasonable.[24]) The energy for rotation might be as large as 5-6 kcal/mol, the relative energy of the butane conformer with eclipsed methyl groups.[24b] The activation energy for capture of the 1,4-diradical by monomer probably is near the activation energy for the chain propagation step, E_p, of PFS. Although the E_p value for PFS is not known, $(E_p - \frac{1}{2}E_t)$ for PFS is about 6 kcal/mol,[25] almost identical with that for styrene,[26] suggesting that the activation energy for propagation for PFS is close to the value of 7 kcal/mol reported for styrene. Thus, the activation energy for ring closure could be 1-2 kcal/mol smaller than that for capture of the 1,4-diradical by monomer. The preexponential for capture should be normal;[24] however, that for ring closure might be some 10^3-10^5 smaller than normal. The uncertainties in these data are such that it would not be impossible for ring closure of the 1,4-diradical **3** and its capture by monomer to have nearly the same rate at 60-100 °C.

An indication of the moles of 1,4-diradical required to produce a given yield of polymer can be obtained by examination of the ratio of yields of DCB to polymer. For styrene and for 2-vinylthiophene, two monomers for which data are available,[27] this ratio is 5:1 and 2000:1, respectively. Thus, even when the Diels-Alder route for polymer formation is available, an appreciative fraction of the monomer forms 1,4-diradicals. Unfortunately, we do not know the ratio of DCB to polymer for PFS. However, the ratio of DCB to polymer might be expected to be even greater for PFS than for 2-vinylthiophene, since diradical production should be facile[14] and the Diels-Alder reaction does not occur. If we arbitrarily assume that this ratio for PFS is 2000-to-1, then the ratio of rates I and II



for PFS is 2000:1 if all initiation is by 1,4-diradicals. Since we have argued above that this ratio might be as great as 1:1 for the trans diradical, **3**, it does not appear to be impossible that the apparent ratio could be 2000:1 for all diradical conformations.

Summary

There must be more than one mechanism for the initiation of the spontaneous polymerization of vinyl monomers. This is indicated by varying ratios of polymer/dimer/trimer, by varying kinetics for reactions with scavengers, and by normal or accelerated polymerization rates on chain transfer. Styrene mainly follows the Diels-Alder mechanism, eq a-c-g in Figure 1A. Pentafluorostyrene (and perhaps methyl methacrylate) are initiated by 1,4-diradicals, Figure 1B; these diradicals react with chain transfer agents (eq k-m) in competition with closure to form cyclobutane derivates (eq j).

Acknowledgment. The research reported here is the result of efforts by a group of students. Most notably, Dr. Bak Kang, a post-doctoral supported on a Dow Research Grant, began the synthetic endeavors and Bernard D. Eble, Jr., an undergraduate research student, brought them to fruition. We want to express our thanks for support to Dow Chemical Company, and to the National Science Foundation for research grants to William A. Pryor, and to Professor K. N. Houk for stimulating discussion.

References and Notes

(1) Part 1. W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Am. Chem. Soc.*, **96**, 5591 (1974).
(2) Part 2. W. A. Pryor and W. H. Hendrickson, Jr., *J. Am. Chem. Soc.*, **97**, 1580 (1975).
(3) Part 3. W. A. Pryor and W. H. Hendrickson, Jr., *J. Am. Chem. Soc.*, **97**, 1582 (1975).
(4) For a review, see: W. A. Pryor and L. D. Lasswell, "Advances in Free Radical Chemistry", Vol. 5 G. Williams, Ed., Academic Press, New York, N.Y., 1975, pp 27-99; (a) pp 78 ff; (b) p 91; (c) p 87; (d) pp 83 ff; (e) p 64; (f) pp 85-87; (g) p 59; (h) footnote *c*, p 85, and p 88; (i) pp 68 ff; (j) p 51; (k) pp 29, 66 ff.
(5) C. Walling and E. P. Briggs, *J. Am. Chem. Soc.*, **68**, 1141 (1946).
(6) (a) Many substituted styrenes[4] and a few nonstyrene monomers such as methyl methacrylate[5] undergo thermal polymerization. All of the various fluorostyrenes which have been studied undergo thermal polymerization, including perfluorostyrene, although those which have fluorines on the side chain require high pressure.[6b] (b) L. W. Wall, "High Pressure Polymerization", National Bureau of Standards Report, July 1970; L. A. Wall and D. W. Brown, *J. Fluorine Chem.*, **2**, 73 (1972/73); D. W. Brown and R. E. Lowry, private communication, 1974.
(7) W. A. Pryor, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **12**, 49 (1971).
(8) W. A. Pryor and J. H. Coco, *Macromolecules*, **3**, 500 (1970).
(9) W. A. Pryor and T. L. Huang, *Macromolecules*, **2**, 70 (1969).
(10) W. A. Pryor and L. D. Lasswell, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **11**, 713 (1970).
(11) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, pp 118-126, 184-186.
(12) P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).
(13) All the isotope data are reviewed and compared in ref 4, p 64. The value of k_H/k_D for styrene-β,β-d_2 is about 0.9, rather than 2-4 as required for eq 3-4.
(14) (a) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968); (b) P. D. Bartlett, *Science*, **159**, 833 (1968); (c) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and G. E. H. Wallbilich, *J. Am. Chem. Soc.*, **91**, 405 (1969); (d) P. D. Bartlett and G. E. H. Wallbilich, *J. Am. Chem. Soc.*, **91**, 409 (1969); (e) P. D. Bartlett, *Pure Appl. Chem.*, **4**, 281 (1971).
(15) C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 432 (1960).
(16) R. Taylor, *J. Chem. Soc. B*, 255 (1971).
(17) P. D. Barlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).
(18) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).
(19) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).
(20) K. E. Russell and A. V. Tobolsky, *J. Am. Chem. Soc.*, **75**, 5052 (1953).
(21) W. A. Pryor and R. W. Henderson, *Int. J. Chem. Kinet.*, **4**, 325 (1972).
(22) Our older data on PFS did not reveal this cross-linking process. Firstly, as we have already reported,[4h] the PFS supplied in 1973-1976 was purer (by GLC analysis) than the material we had obtained prior to 1969. Secondly, most of the data in the 1969 report[9] pertain to the initiated polymerization. Cross-linking due to eq 15 would not be observeable as readily, if at all, in initiated polymerizations, since the major polymer-end-forming process there is initiation rather than transfer as is true in thermal polymerizations.[8] Thirdly, most of our older data involve use of toluene, THF, or dioxane as solvents, and these relatively good transfer agents would protect the polymer from undergoing the transfer cross-linking process.
(23) See Table IV, ref 9.
(24) (a) See, for example, M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 5246 (1974), and references cited therein; (b) L. M. Stephensson and T. A. Gibson, *Ibid.*, **94**, 4599 (1972).
(25) T. L. Huang, Dissertation, LSU, 1970; W. A. Pryor and T. L. Huang, unpublished data.
(26) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y. 1957, p 95.
(27) This argument is related to one we have made for the styrene case; p 75 in ref 4.