tem at 60° using gel permeation chromatography (gpc). They are able to calculate values of C, C_M, and k_t/k_p^2 from the molecular weight distributions obtained by gpc. They obtain a transfer constant for AIBN which is about 0.16. This value is even larger than the value we have found. Part of the discrepancy between our value and theirs is due to the use of different values of C_M and k_t/k_p^2. They find a "best fit" value of k_t/k_p^2 of 646, and this leads to C_M of 9×10^{-5} and C of 0.16. However, if they use a value of k_t/k_p^2 of 800, which is closer to the value of 900 used here, they obtain $C = 0.07$, which is fairly close to our value of 0.02. Their technique and analysis is entirely independent of ours, and we regard it as significant that the two methods give values for C for AIBN which are of the same order of magnitude.

The Kinetics of the Polymerization of Pentafluorostyrene[1,2]

William A. Pryor and Tzu-Lee Huang

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

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ABSTRACT: Data are reported on the thermal and AIBN-initiated polymerization of 2,3,4,5,6-pentafluorostyrene (PFS) both neat and in the presence of solvents. Comparison of molecular weights determined osmometrically with those obtained using tritium-labeled AIBN indicates that termination occurs largely by combination. Molecular weights could be calculated from intrinsic viscosities using the equation $\overline{M}_n = 8.50 \times 10^5[\eta]^{1.36}$. Intrinsics were obtained both by the usual dilution technique and also from the equation $[\eta] = \{[1 + 2.08\eta_{sp}]^{1/2} - 1\}/0.75C_v$, where C_v is the concentration in methyl isobutyl ketone at 30° in grams per 100 ml. The solubility of poly-PFS is reported in a large number of solvents. Values of $2k_d f/\delta^2$ are reported for the AIBN-initiated polymerization in several solvents. From these values and molecular weight data, values of f and δ^2 are 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. This is 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 the monomer. If this mechanism were to apply to PFS, a fluorine atom would have to be transferred. The transfer constant of PFS is zero; this fact also is relevant to the speculation on the mechanism of thermal initiation. Transfer to THF, fluorobenzene, methyl isobutyl ketone, and methyl isopropyl ketone was studied in binary mixtures with PFS, and transfer to the nonsolvents cumene, ethylbenzene, toluene, chlorobenzene, and bromobenzene was studied in the presence of either THF or fluorobenzene as a third solvent to solubilize the poly-PFS. Transfer constants are reported and are compared to those for styrene. As expected from the polar character of PFS, transfer constants for the ketones are smaller for PFS than for styrene, whereas those for toluenelike hydrocarbons are larger for PFS. The copolymerization of PFS with styrene and with methyl methacrylate has been 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 0.90, 0.75, and 0.87. The kinetics of the copolymerizations have also been examined: for PFS–styrene, ϕ is 7.2 and for MMA it is 5.3.

The compound 2,3,4,5,6-pentafluorostyrene (PFS) was synthesized for the first time in 1959 by Wall[3a] in the United States and by Nield, *et al.*,[3b] in England and is now available commercially from several suppliers. We here report a study of the radical-initiated polymerization of this interesting vinyl monomer. Both polymerization initiated by azobisisobutyronitrile (AIBN) and the self-initiated, "thermal" polymerization have been examined.

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 pure monomer has bp 141–142° (760 mm)[3] and n^{20}_D 1.4410–1.4420.

Isolation of the Polymer. Polymer was isolated by a modification of the freeze-dry procedure developed by Lewis and Mayo for styrene;[4] 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 using 50–100 ml of tetrahydrofuran (THF), the solvent was pumped off under a moderate vacuum, 50 ml of benzene was added, and 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.

Some runs using tritium-labeled AIBN were performed. When radioactive initiator was used, 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 poly-

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(1) Reactions of Radicals. Part XVIII.

(2) This research was partially supported by a grant from the U. S. Army Research Office, Durham, N. C.

(3) (a) W. J. Plummer and L. A. Wall, *J. Res. Nat. Bur. Stand.*, **63A**, 167 (1959); (b) E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959).

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

TABLE I

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°)	Convn, %	$R_{P,obsd} \times 10^5$[c]	$R_P \times 10^5$[d]	$[\eta]$	$10^4/\bar{P}$
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		
None	7.01	92.5	0.674	2	8.84	8.99	8.99		
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	3.48	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
THF	3.30	9.24	0.100	20	19.9	1.01	1.01	0.57	4.80
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		

[a] Solutions consist of PFS and AIBN plus the third component listed. Solvents are 50% by volume. [b] PFS in moles per liter-the molarities shown are average molarities which have been corrected for per cent conversion. [c] Observed rate of polymerization in M^{-1} sec^{-1}. [d] $R_P = [R_{P,obsd}^2 - R_{P,th}^2]^{1/2}$; $R_{P,th} = 0.570 \times 10^{-6}\ M^{-1}$ sec^{-1}.

merized 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. Molecular weights were measured using a Hewlett-Packard Model 501 membrane osmometer. Conditions were 30°, S&S 0–8 membrane, and methyl isobutyl ketone (MIBK) as solvent. Molecular weights were also measured by counting polymer prepared using tritium-labeled AIBN[5a] as initiator and 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 using fluorobenzene as a solvent. Counting was done using 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[5b] 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 0.05–0.07 g/25 ml of MIBK. Intrinsic viscosities were determined by extrapolation of specific viscosities to infinite dilution. Intrinsics could also be calculated using

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

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

Kinetics. Rates of thermal and catalyzed polymerizations were followed using either a 10-ml dilatometer or by an ampoule technique. The density of PFS was found to be 1.414 g/ml at 30°, 1.388 g/ml at 46.2°, and 1.366 g/ml at 60°. The plot of per cent polymer in monomer (*i.e.*, per cent conversion) *vs.* density is linear to about 25% conversion, our highest calibration point. Our data at 60° give the relation: per cent conversion = (0.1040)(per cent contraction). This relation is similar to that for other substituted styrenes.[6a,b] Our density measurements on polymer–monomer mixtures extrapolate to give 1.5921 g/ml for the density of poly-PFS at 100% conversion. We have measured the density of the polymer by pressing it under 90,000 psi, placing it in a pycnometer which is 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 1.5499 g/ml. This density of the solid polymer is about 2.6% less than that calculated for an infinitely concentrated solution

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(5) (a) W. A. Pryor and T. R. Fiske, *Macromolecules*, 2, 62 (1969). (b) Prepared by Dr. T. R. Fiske.

(6) (a) M. Kinoshita and M. Imoto, *Kobunshi Kagaku*, 20, 231 (1963); (b) M. Kinoshita, *ibid.*, 20, 237 (1963); *Kogyo Kagaku Zasshi*, 66, 982 (1963); (c) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Amer. Chem. Soc.*, 73, 1700 (1951); also see W. M. Thomas, E. H. Gleeson, and J. J. Pellon, *J. Polym. Sci.*, 17, 275 (1955).

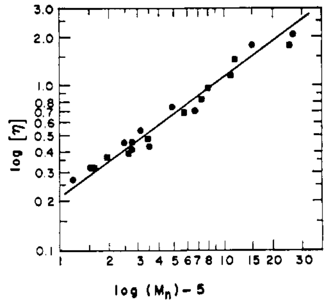


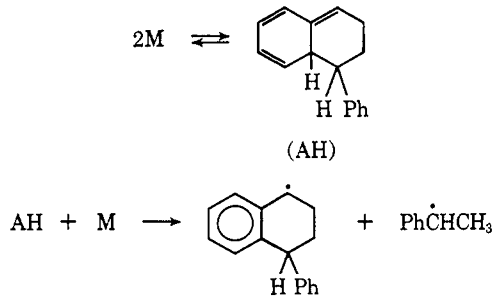
Figure 1. Intrinsic viscosity in MIBK at 30° for poly-PFS *vs.* molecular weight: ●, data obtained by osmometry; ■, data obtained using tritiated AIBN and assuming that termination is entirely by combination.

of polymer in its own monomer. Similar behavior has been reported for styrene.[6c]

Solubility. Poly-PFS has the following solubilities: it is soluble in methyl ethyl ketone, methyl isobutyl ketone, THF, ethyl acetate, and fluorobenzene; slowly soluble or slightly soluble in pyridine, acetone, methyl isopropyl ketone, and chlorobenzene; and insoluble in benzene, toluene, iodobenzene, bromobenzene, CCl_4, $CHCl_3$, CS_2, methanol, ethanol, ether, tetralin, dioxane, decalin, cyclohexane, hexane, heptane, and *o*-dichlorobenzene.

Results and Discussion

Thermal Polymerization. The purified monomer gave a reproducible rate of uninitiated polymerization at 60° of 5.70×10^{-7} M^{-1} sec^{-1} (0.0280%/hr). For comparison, the thermal rate for styrene[7c] at 60° is 2.06×10^{-6} M^{-1} sec^{-1} (0.10%/hr). The mechanism for the spontaneous initiation of polymerization of styrene which has received the most support is that first postulated by Mayo.[7] It involves a reversible Diels–Alder condensation of two styrenes to form an adduct, AH, which then transfers a hydrogen to another styrene molecule.[8] If an analogous mechanism applies to PFS, then a fluorine atom must be transferred; this certainly would be novel, and we intend to investigate the thermal polymerization of PFS further.



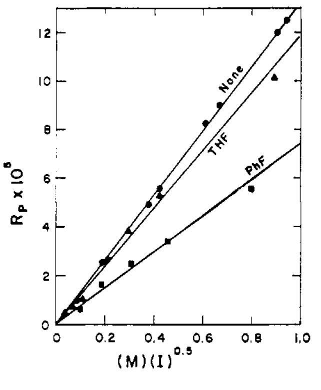


Figure 2. Graph of eq 4 for the AIBN-initiated polymerization of PFS at 60°. Solvents (50% by volume) are coded as follows: ●, none; ▲, THF; ■, fluorobenzene. Data for pyridine as solvent are not shown; they lie very near the line for pure PFS.

Molecular Weights. Molecular weights for poly-PFS ranged downward from 6.8 million for thermal polymer prepared at 60°. Table I gives data for the polymerization of PFS under a number of experimental conditions. Figure 1 shows the relationship between the number-average molecular weight, $\bar{M}_n$, and the intrinsic viscosity. Molecular weights were measured both by osmometry and by counting polymer prepared in the presence of AIBN-*t* assuming that termination is entirely by combination. The agreement between the two methods (see Figure 1) shows that termination is entirely by combination within the accuracy of our molecular weight measurements. The line shown in Figure 1 yields the equations $[\eta] = 4.37 \times 10^{-5} \bar{M}_n^{0.736}$, or, $\bar{M}_n = 8.50 \times 10^5[\eta]^{1.36}$. Methyl isobutyl ketone (MIBK) is nearly a Θ solvent for poly-PFS and is convenient for osmometry and viscosity measurements.

Catalyzed Polymerization. The equations for the polymerization of a vinyl monomer are[6a]

$$I \xrightarrow{k_d f} 2R\bullet$$

$$R\bullet + M \xrightarrow{k_a} M\bullet$$

$$M\bullet + M \xrightarrow{k_p} M\bullet$$

$$2M\bullet \xrightarrow{k_t} \text{polymer}$$

where I is the initiator, M is PFS, termination is by combination, and reactivity is assumed to be independent of chain length. For a monomer with an appreciable thermal rate

$$R_{P,\text{obsd}}^2 = R_{P,\text{th}}^2 + R_P^2 \qquad (1)$$

Using the conventions

$$R_i = 2k_d f(\text{I}) \qquad (2)$$

$$R_t = 2k_t(\text{M}\bullet)^2 \qquad (3)$$

the usual steady state conditions give the relation

$$R_P = (2k_d f/\delta^2)^{0.5}(\text{M})(\text{I})^{0.5} \qquad (4)$$

where $\delta^2 = 2k_t/k_p^2$ and parentheses indicate concentrations in moles per liter.

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(7) (a) F. R. Mayo, *J. Amer. Chem. Soc.*, **75**, 6133 (1953); (b) *ibid.*, **90**, 1289 (1968); (c) W. A. Pryor, R. Henderson, N. Carroll, and E. Ciuffarin, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 7s; (d) R. H. Boundy and R. F. Boyer, "Styrene," Reinhold Publishing Corp., New York, N.Y., 1952, pp 216–222.

(8) W. A. Pryor, *Chem. Eng. News*, **46**, 80 (Jan 15, 1968).

Table I gives data for the AIBN-initiated polymerization of PFS both neat and in the presence of a number of cosolvents. Figure 2 shows these data plotted in the form of eq 4; the slopes of the lines yield values of $2k_df/\delta^2$, and the second column of Table II gives these values. A value for f may be obtained from the molecular weights of the polymers in the following manner.[9,10] Since termination is by combination, the kinetic chain length, ν, equals $\bar{P}/2$, and since $\nu = R_P/R_i$[9c]

$$R_i = 2R_P/\bar{P} = 2k_df(\mathrm{I}) \qquad (5)$$

The data in Table I can be plotted in the form $2R_P/\bar{P}$ *vs.* (AIBN) and the result is a straight line with a slope equal to $2k_df$. For example, in pure PFS, the slope gives $R_i = 11.8 \times 11^{-6}$ (AIBN) sec^{-1}. If the value of 1.13×10^{-5} sec^{-1} is taken for k_d at 60°,[11a] 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 the inhibitor method, is 0.55.[11b] Table II gives values of f for AIBN calculated by this method for mixtures of PFS in the other solvent mixtures.

Using these values of f, and the literature value of k_d,[11a] apparent values of δ^2 can be calculated in the solvent mixtures. These data are shown in the last column of Table II. We have previously discussed[12e] the solvent dependence of δ^2. The value of δ^2 of 675 in pure PFS compares with the value of 900 in styrene at 60°.[12] 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,[12] 0.0333; methyl methacrylate,[13a], 0.147; vinyl acetate,[13b] 0.430.

TABLE II
THE POLYMERIZATION OF PFS INITIATED BY AIBN AT 60°

Solvent[a]	$(2k_df/\delta^2) \times 10^8$ [b]	f[c]	Apparent δ^2 [d]
None	1.74	0.52	675
Fluorobenzene	0.548	0.26[e]	1073[e]
THF	1.42	0.29[e]	463[e]
Pyridine	1.74		
Styrene		0.57[f]	
MMA		0.50[g]	

[a] Solvents are 50% by volume. [b] Calculated from the slopes of graphs like Figure 2. [c] Calculated from plots of eq 5 and the value 1.13×10^{-5} for k_d. [d] Calculated from columns 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.

Transfer to Solvents. Transfer to fluorobenzene and THF could be studied in the usual way[9d] since the polymer is soluble in these solvents. In addition, transfer to hydrocarbon solvents was studied using THF as a cosolvent. Equation 6 was used to calculate transfer constants,[9d] where the term due to transfer to

$$\frac{1}{\bar{P}} = \frac{\delta^2}{2(\mathrm{M})^2}R_{\mathrm{P,obsd}} + C_{\mathrm{M}} + C_{\mathrm{I}}\frac{(\mathrm{I})}{(\mathrm{M})} + C_{\mathrm{S}}\frac{(\mathrm{S})}{(\mathrm{M})} + C_{\mathrm{THF}}\frac{(\mathrm{THF})}{(\mathrm{M})} \qquad (6)$$

AIBN, $C_I(\mathrm{I})/(\mathrm{M})$, has been taken as approximately zero,[5a] and S is a variable solvent. Tables III and IV give the data; comparable data for styrene for the solvents THF, MIBK, MIPK, and fluorobenzene were also obtained. It should be noted that in some cases R_P/R_P^0 is larger than 5 where $R_P^0 = R_{P,\mathrm{th}}[(\mathrm{M})/(\mathrm{M})_0]$, $(\mathrm{M})_0$ and (M) being molar concentrations of pure monomer and diluted monomer, respectively, and R_P the observed rate of polymerization. It is necessary to plot

$$\left[\frac{1}{\bar{P}} - \frac{\delta^2}{2(\mathrm{M})^2}R_P - C_M\right]$$

against (S)/(M) in order to obtain the correct values of C_S for these systems.[14f] 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 3 and 4 show plots of eq 6 in the form necessary to determine the transfer constants. Table V compares the transfer constants for PFS with data for styrene. As Table V shows, plots like Figures 3 and 4, which are corrected for enhanced rates of polymerization,[14f] gave the same transfer constant as did the normal Mayo plot for all transfer agents except MIBK. In the case of cumene, both THF and fluorobenzene were used as cosolvents, and the transfer constants obtained for cumene agreed excellently, although in both cases the rate of polymerization was greatly enhanced. The data of Table V 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–

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(9) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co. Inc., New York, N. Y., 1966; (a) pp 234–247; (b) p 237; (c) pp 23–239; (d) pp 244 ff; (e) pp 170–176.

(10) W. A. Pryor and E. P. Pultinas, *J. Amer. Chem. Soc.*, **85** 133 (1963).

(11) (a) J. C. Bevington and H. G. Troth, *Trans. Faraday Soc.*, **58,** 186 (1962); (b) M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86,** 217 (1965).

(12) (a) D. H. Johnson and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **74,** 938 (1952); (b) A. V. Tobolsky and J. Offenbach, *J. Polym. Sci.*, **16,** 311 (1955); (c) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **37,** 71 (1960); (d) W. A. Pryor, A. Lee, and C. E. Witt, *J. Amer. Chem. Soc.*, **86,** 4229 (1964); (e) W. A. Pryor and G. L. Kaplan, *ibid.*, **86,** 4234 (1964).

(13) (a) E. P. Bonsall, L. Valentine, and H. W. Melville, *Trans. Faraday Soc.*, **48,** 763 (1952); (b) M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Amer. Chem. Soc.*, **71,** 2610 (1949); (c) G. V. Schulz and D. J. Stein, *Makromol. Chem.*, **2,** 1 (1962).

(14) (a) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2,** 328 (1947); (b) G. Henrici-Olivé and S. Olivé, *Fortschr.-Hochpolym. Forsch.*, **2,** 496 (1961); (c) W. A. Pryor and T. L. Pickering, *J. Amer. Chem. Soc.*, **84,** 2705 (1962); (d) G. S. Misra and R. N. Chadha, *Makromol. Chem.*, **23,** 134 (1957); (e) S. L. Kapur, *J. Polym. Sci.*, **11,** 399 (1953); (f) T. Huff and E. Perry, *ibid., Part A-1*, 1553 (1963).

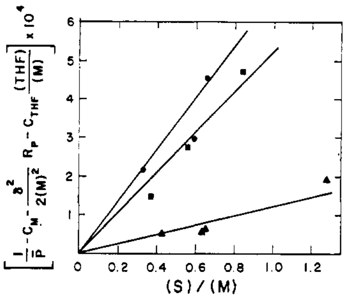

Figure 3. Transfer to cumene (●), ethylbenzene (■), and toluene (▲) by PFS at 60° in the presence of the cosolvent THF.

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.[9e] As expected, the PFS radical

$$\underset{\text{I}}{M_n\bullet\ H{-}S} \qquad \underset{\text{II}}{M_n^+\ \dot{H}\ ^-{:}S} \qquad \underset{\text{III}}{M_n{:}^-\ \dot{H}\ ^+S}$$

is much less able to bear positive charge as required in dipolar form II than is the polystyryl radical. Thus the polystyryl has enhanced transfer constants to the ketones relative to toluene, whereas the reverse is true of the radical from PFS. The apparent transfer constant for monomer is smaller for PFS than for styrene. There is uncertainty at present over the meaning of the apparent transfer constant for styrene monomer. The usually accepted value is much too high when compared to model compounds. Müller[15] has suggested that transfer actually occurs to the Diels–Alder adduct of styrene with itself. If this is the case, then either PFS forms lower concentrations of dimer or its dimer has a smaller transfer constant. Either or both might be expected to be the case, but the similar rates of thermal polymerization of PFS and styrene are then difficult to rationalize with the mechanism involving a Diels–Alder dimer.

Transfer was also studied using AIBN-initiated polymerization, and the data agree well with those from thermal polymerizations. (The data are shown in Table I.) Plots of eq 6 for the data for fluorobenzene show the transfer constant of PFS to be zero. 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.

Copolymerization of PFS and Styrene. Styrene and PFS were allowed to copolymerize at 60°. Copolymer composition was evaluated using per cent carbon from elemental analysis.[16] The copolymerization equation is[17]

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\,\frac{r_1M_1 + M_2}{r_2M_2 + M_1} \tag{7}$$

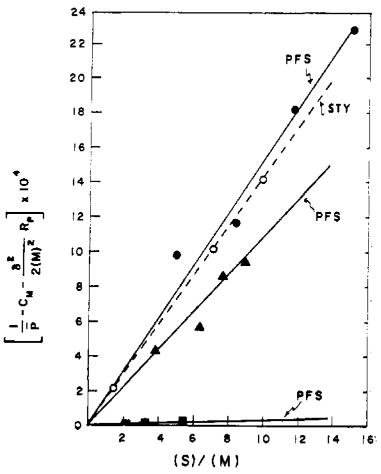

Figure 4. Transfer to THF (●), MIPK (▲), and MIBK (■) by PFS (filled symbols) and to THF by styrene (open circles).

The technique of Fineman–Ross[18] was used to evaluate r_1 and r_2; their equation is

$$\frac{F}{f}(f - 1) = r_1F^2/f - r_2 \tag{8}$$

where $f = dM_1/dM_2$, $F = M_1/M_2$, monomer 1 is styrene and PFS is monomer 2. Table VI gives the data; the values of $r_1 = 0.43$ and $r_2 = 0.22$ are obtained from the Fineman–Ross graph (least square fit of data). These data are compared with values for pentachlorostyrene[19–21] and *p*-fluorostyrene[19] in Table VII. 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 Alfrey–Price equations (eq 9 and 10) and the

$$e_2 = e_1 \pm (-\ln r_1r_2)^{0.5} \tag{9}$$

$$Q_2 = \frac{Q_1}{r_1}\exp[-e_1(e_1 - e_2)] \tag{10}$$

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.

The copolymerization was also studied at 60° using AIBN initiation to determine the value of the cross-termination ratio ϕ. The equation is

$$R_P = \frac{[r_1M_1^2 + 2M_1M_2 + r_2M_2^2]R_i^{0.5}}{[r_1^2\delta_1^2M_1^2 + 2\phi r_1r_2\delta_1\delta_2M_1M_2 + r_2^2\delta_2^2M_2^2]^{0.5}} \tag{11}$$

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $\delta_1^2 = 2k_{t11}/k_{11}^2$, $\delta_2^2 = 2k_{t22}/k_{22}^2$, and $\phi = k_{t12}/2(k_{t11}k_{t22})^{1/2}$. Table VI gives

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(15) K. F. Müller, *Makromol. Chem.*, **79**, 128 (1964).

(16) The fraction styrene in the copolymer, f_2, 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 $f_2 = (194.1x - 96.079)/(90.0x - 0.036) \cong 2.157 - 1.067/x$.

(17) See ref 9, p 243.

(18) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

(19) "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience Publishers, New York, N. Y., 1966.

(20) T. Alfrey, Jr., and W. H. Ebelke [*J. Amer. Chem. Soc.*, **71**, 3235 (1949)] give data calculated using the older values of $Q = 1.00$ and $e = -1.0$ for styrene. These data have been recalculated by L. J. Young (see ref 19 and 21) using the newer values for styrene of $Q = 1.00$ and $e = -0.8$.

(21) L. J. Young, *J. Polym. Sci.*, **54**, 411 (1961).

TABLE III

THERMAL POLYMERIZATION OF PFS IN THF, FLUOROBENZENE, MIBK AND MIPK AT 60°

(S)/(M)	(M)	Time, hr (at 60°)	Convn, %	R_P/R_P^0 [a]	$10^5/\bar{P}$	$\left[\frac{1}{\bar{P}} - C_M - \frac{\delta^2}{2(M)^2}R_P\right] \times 10^4$ [b]
			No Solvent			
0	7.33	163	4.74	(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
			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	
			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
			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

[a] $R_P^0 = R_{P,th}(M)/7.33$ where $R_{Pth} = 0.0280\%$/hr for pure PFS at 60°, R_P is the observed rate of polymerization in per cent per hour. [b] Calculated by assuming $C_M = 0$ and $\delta^2 = 463$ for THF and $\delta^2 = 675$ for MIBK and MIPK solutions.

TABLE IV

THERMAL POLYMERIZATION OF PFS IN MIXED SOLVENTS CONSISTING OF THF AND THIRD COMPONENT

(S)/(M)	(THF)/(M)	(M)	Time, hr (at 60°)	Convn, %	R_P/R_P^0 [a]	$\left[\frac{1}{\bar{P}} - C_{THF}\frac{(THF)}{(M)}\right] \times 10^4$ [b]	$\left[\frac{1}{\bar{P}} - C_M\frac{\delta^2}{2(M)^2}R_P - C_{THF}\frac{(THF)}{(M)}\right] \times 10^4$ [c]
				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
				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
0.642	10.1	0.977	35	6.82	52.3	1.90	0.62
1.28	5.02	1.47	24	3.64	27.1	2.87	1.90
				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	

[a] See footnote *a* in Table III. [b] The transfer constant of THF was taken as 1.53×10^{-4}. [c] Calculated by assuming $C_M = 0$ and $\delta^2 = 463$ (See Table II). [d] Fluorobenzene used as the cosolvent rather than THF; its transfer constant was taken as 1.17×10^{-5}.

Table V

A Comparison of the Transfer Constants for PFS and Styrene toward Several Solvents at 60°[a]

Solvent	$C \times 10^4$	
	PFS	Styrene
THF	1.53 (1.54)	1.44 (1.62)[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]
Methyl isobutyl ketone (MIBK)	0.033 (0.287)	0.767[b]
Methyl isopropyl ketone (MIPK)	1.09 (1.14)	2.41[b]
Fluorobenzene	0.117	0.0372[b]
Chlorobenzene	~0[e]	0.133[f]
Bromobenzene	~0[e]	1.78[g]

[a] Figures not in parentheses are obtained from plots like Figures 3 or 4 in cases where $R_P/R_P{}^\circ$ was greater than 5. The numbers in parentheses were determined from the ordinary Mayo plot. [b] Determined here. All values are computed from least square fits of eq 6. [c] Recalculated by Henrici-Olivé[14b] from data of Mayo.[14a] [d] Determined in the presence of the cosolvent THF. [e] Determined in the presence of the cosolvent fluorobenzene. [f] Determined by Misra and Chadha.[14d] [g] Determined by Kapur.[14e] [h] Using fluorobenzene instead of THF as cosolvent gives $C = 6.82 \times 10^{-4}$

the data. A value of $\phi = 7.2$ is found, indicating a substantial tendency toward cross-termination.[22-24]

Copolymerization of PFS and Methyl Methacrylate. The same procedures were followed in evaluating copolymerization parameters for methyl methacrylate and PFS. The composition of the copolymer was determined using ultraviolet spectroscopy. Table VIII gives the data.[25] The Fineman-Ross treatment yields $r_1 = 0.98$ and $r_2 = 0.90$, where M_1 is MMA and M_2 is PFS. Using $Q_1 = 0.74$ and $e_1 = 0.40$,[21] 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 VIII also gives rate data, and the value of $\phi = 5.3$ is obtained.

Table IX 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.[19] The average value of Q of 0.78 for PFS can be compared with 1.00 for styrene, 0.83 for *p*-

Table VI

Copolymerization of PFS (M_2) and Styrene (M_1) at 60°[a]

(M_1)	(M_2)	Rate × 10^5 [b]	Polymer composn, % M_2[c]	f	F	ϕ[d]
8.71	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			

[a] In presence of 8.85×10^{-3} *M* AIBN. [b] In *M* sec^{-1}. [c] From per cent carbon in copolymer. Analysis by nmr in carbon tetrachloride was less precise but gave data consistent with these. [d] The following values were used: M_1 = styrene; M_2 = PFS; $r_1 = 0.43$; $r_2 = 0.22$; $\delta_1{}^2 = 900$; $\delta_2{}^2 = 675$; $R_i = 2k_d f$(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 II) and in a 50/50 mixture of styrene and PFS to be 0.57; f in pure styrene is 0.60 (ref 11a). In all the calculations in Table VI, f was taken as 0.57. Variation of f between 0.52 and 0.60 does not appreciably affect the value of ϕ.

Table VII

Copolymerization Parameters for Several Monomers with Styrene (M_1)

M_2	r_1	r_2	$1/r_1$	Q_2	e_2	Ref
Pentachlorostyrene	1.31	0.35	0.7	0.22	0.52	*a, b*
p-Fluorostyrene	0.7	0.9	1.4	0.83	−0.12	*a*
PFS	0.43	0.22	2.3	0.69	0.74	Here

[a] See ref 21. [b] See ref 20.

Table VIII

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

Run no.	(M_1)	(M_2)	Rate × 10^5	Polymer composn, % M_2[b]	f	F	ϕ[c]
1	9.35	0	29.5	0			
2	7.79	1.22	17.4	14.9			6.0
3	7.01	1.83	16.4	20.6	3.85	3.83	4.5
4	6.23	2.44	13.1	27.4	2.65	2.55	5.7
5	4.68	3.66	11.9	44.8	1.23	1.28	4.6
6	2.34	5.50	9.92	67.8	0.475	0.425	4.5
7	1.56	6.11	8.77	79.1	0.264	0.255	6.5
8	0	7.33	7.66	100			

[a] In presence of 8.85×10^{-3} *M* AIBN. [b] From uv spectroscopy. [c] Calculated using $r_1 = 0.98$; $r_2 = 0.90$; $\delta_1{}^2 = 46.2$ (E. P. Bonsall, L. Valentine, and H. M. Melville, *Trans. Faraday Soc.*, **48,** 763 (1952)); $\delta_2{}^2 = 675$; $R_i = 2k_d f$ (AIBN) with $k_d f = (1.13 \times 10^{-5})$ (0.50) sec^{-1}. The following values of f have been measured: 0.52 in pure PFS; 0.50 in an 50:50 mixture of PFS and MMA; 0.46 in pure MMA (G. M. Burnett, W. S. Dailey, and J. M. Pearson, *Trans. Faraday Soc.*, **61,** 1216 (1965)). The variation of f between 0.52 and 0.46 affects the value of ϕ by less than 8%.

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(22) See Table VI, footnote *d*.

(23) The definition and the use of the factor of 2 in δ_1, δ_2, and R_i are those used by Walling (ref 24, pp 100, 144–145) and ourselves (ref 9, pp 14, 315). However, we have also used the usual American definition of ϕ given by Walling (ref 24, p 145) rather than the alternative English convention (ref 9, p 315). In this American convention, the expected value of ϕ is 1.

(24) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957.

(25) In THF as a solvent, the specific absorbance for PFS (in units of absorbance per mole per liter) is $\epsilon = 1.92$ at λ_{max} 259 mμ and is independent of molecular weight. Beer's law is obeyed. At this wavelength, MMA has ϵ 0.095. The equation used is $\epsilon = 1.92x + (1 - x)(0.095)$, where x is the weight fraction of PFS in the copolymer.

TABLE IX
A SUMMARY OF THE COPOLYMERIZATION PARAMETERS FOR PFS

M_1	M_2	r_1	r_2	Q_2	e_2	r_1r_2	ϕ
Styrene	PFS	0.43	0.22	0.69	0.74	0.095	7.2
Methyl meth-acrylate	PFS	0.98	0.90	0.87	0.75	0.89	5.3

fluorostyrene, and 0.22 for pentachlorostyrene.[19] Alfrey and Ebelke[20] 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.[26]

It is usually expected that a large tendency toward alternation of monomers in a copolymer will be reflected in a large value of ϕ. The data of Table IX do not accord with this expectation; the styrene copolymer, which is appreciably alternating, has a rather small ϕ value. Table X summarizes similar data for the literature. Walling[27] found that the ϕ 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 factors than is the more activated addition to a double bond.

TABLE X
VALUES OF THE CROSS-TERMINATION CONSTANT ϕ

System	ϕ	r_1/r_2
PFS–styrene[a]	7.2	0.095
PFS–MMA[a]	5.3	0.89
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

[a] Present value. [b] G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, New York, N.Y., 1954, pp 295–297. [c] See ref 27.

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(26) Atomic radii (ångströms) are H, 0.28; F, 0.64; Cl, 0.99: "Tables of Interatomic Distance and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London.

(27) C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.*, 73, 2819 (1951).

Simultaneous Cationic Homopolymerizations of Vinylcarbazole and Oxetane

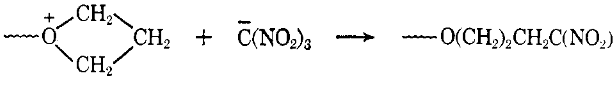
R. Gumbs, S. Penczek, J. Jagur-Grodzinski, and M. Szwarc

Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received August 21, 1968*

ABSTRACT: Polymerization of vinylcarbazole and oxetane was initiated in nitrobenzene by tetranitromethane (TNM). It was shown that nitroform is the probable initiator, the latter being formed by the sequence

$$C(NO_2)_4 + CH_2{=}CHN< \rightarrow C(NO_2)_3^- + NO_2CH_2CH^+N< \rightarrow HC(NO_2)_3 + NO_2CH{=}CHN<$$

The uptake of both monomers was followed by nmr technique; thus $-d[V]/dt$ and $-d[Ox]/dt$ were determined simultaneously. The reaction produces a mixture of two homopolymers. Although the presence of oxetane reduced the rate of vinylcarbazole polymerization by a factor of 30, it did not affect its molecular weight. The polymerization of vinylcarbazole is first order in TNM and in monomer; the termination apparently involves a "wrong" monomer addition. The polymerization of oxetane requires the presence of vinylcarbazole; TNM alone does not initiate the reaction. Its rate is proportional to $[TNM]^{1/2}$, $[V]^{1/2}$ and [Ox], indicating bimolecular termination arising from combination of the ions. The kinetic results demonstrate that oxetane is about 30 times more reactive toward nitroform than vinylcarbazole.



Polymerization of vinylcarbazole initiated in nitrobenzene by tetranitromethane was studied by Pac and Plesch,[1] who found the reaction to be first order in the initiator and monomer. The molecular weight of the resulting polymer was independent of the concentration of the initiator but increased with concentration of the monomer. The following mechanism was proposed. Tetranitromethane (TNM) and vinylcarbazole (V) form reversibly charge-transfer complex which slowly decomposes into positive $(V)\cdot^+$ and negative $(TNM)\cdot^-$ radical ions. The former initiate cationic polymerization, namely

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(1) J. Pac and P. H. Plesch, *Polymer*, 8, 252 (1967).