Studies of Primary Radical Termination in Vinyl Polymerization. The Polymerization of Styrene Initiated by Tritium-Labeled Azobisisobutyronitrile. Measure of the Transfer Constant of Azobisisobutyronitrile[1]

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ABSTRACT: It is generally agreed that primary radical termination (PRT) is one of the most important causes of deviations of the kinetics of vinyl polymerizations from the kinetic laws predicted from the "simple" system of equations. (Primary radical termination is the reaction in which primary radicals from the initiator terminate growing chains rather than adding to monomer to initiate chain growth.) One of the systems in which PRT has been studied in the greatest detail is the polymerization of styrene initiated by azobisisobutyronitrile (AIBN). We have attempted to determine the number of end groups due to primary radical termination in this system using a radiotracer technique. To do this, it is necessary to know the transfer constant of AIBN; this transfer constant has been reported to be zero by four groups of workers. Data are here reported on the polymerization of styrene at 60° in the presence of a constant amount of tritium-labeled AIBN and a variable amount of inactive AIBN. The data are treated according to the equation $R^* = k_d f(\mathrm{I}^*) + C[(\mathrm{I}^*)/(\mathrm{M})]R_\mathrm{P}$,[3] where R^* is the rate of incorporation of AIBN-*t* into the polymer, (I^*) is the concentration of labeled AIBN, (M) is that of styrene, k_d is the rate constant for decomposition of AIBN, f is its efficiency, C is the transfer constant of AIBN, and R_P is the rate of formation of polymer. A plot of R^* *vs.* R_P can yield values of $k_d f$ and C. In contrast with the previous reports, our data yield an apparent value for C which is substantial. Possible systematic errors in the tracer method for measuring the transfer constant of AIBN are discussed; for example, copolymerization of the AIBN would lead to an apparent transfer constant. However, experiments have been done which appear to rule out copolymerization and other alternative explanations. Thus it appears that AIBN does have an appreciable transfer constant. The implications of this for studying PRT by this method are discussed.

There are several chain-end forming processes which are important in the initiated polymerization of a vinyl monomer. These include the formation of chain ends by the addition of radicals from the initiator to the monomer to initiate growth, transfer to the monomer, transfer to the initiator, and transfer to any solvent which might be present. These chain-ending processes are well known, and their features have been described in most standard texts.[4-8] Additionally, it has recently been suggested that another process, called primary radical termination, becomes important at high rates of polymerization or low monomer concentrations.[9] In this process, primary radicals from the initiator combine with a growing polymer chain and stop growth, rather than adding to monomer to initiate a chain.

It is convenient to tabulate chain ends from these processes in units of $1/\bar{P}$, where $\bar{P}$ is the number-average degree of polymerization and has the units $\bar{P} = [-\mathrm{d(M)}/\mathrm{d}t]/[+\mathrm{d(polymer)}/\mathrm{d}t]$ = monomer units per polymer molecule. Thus we can qualitatively tabulate the sources of chain ends as

$$1/\bar{P} = \text{terms due to initiation, transfer to monomer, transfer to initiator, and PRT} \qquad (1)$$

where PRT indicates primary radical termination, and where the polymerization is carried to low conversions where transfer to the polymer is negligible and no added solvent is present.

The work which we describe here was begun in the hope of applying a sensitive tracer technique to measuring the number of end groups due to PRT at various monomer concentrations and rates of polymerization. This is important, since it is generally agreed that primary radical termination is a likely source of most of the deviations from the predictions based on the "simple" kinetic scheme for polymerization.[7b,8b] For our study, and following earlier workers in the field, we elected to use the thoroughly studied system styrene and azobisisobutyronitrile (AIBN). At first we assumed, as had previous workers, that the transfer constant of AIBN was zero. In fact, four groups of workers had measured the transfer constant of AIBN and reported it to be effectively zero.[10-13] We found,

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(1) (a) Reactions of Radicals. XVI. (b) We wish to acknowledge partial support of this work by the U. S. Army Research Office (Durham).

(2) (a) Abstracted in part from the Ph.D. Dissertation of T. R. Fiske, Louisiana State University, Jan 1968. (b) Dow Chemical Company Fellow in Polymer Chemistry.

(3) W. A. Pryor, *J. Phys. Chem.*, **67**, 519, 2889 (1963).

(4) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1966, pp 234–247.

(5) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 64–82.

(6) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 136–145.

(7) M. H. George in "Vinyl Polymerization," Part I, Vol. 1, G. E. Ham, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, (a) pp 142–169; (b) pp 161, 162.

(8) J. C. Bevington, "Radical Polymerization," Academic Press, New York, N. Y., 1961, (a) pp 102–132; (b) pp 148–152.

(9) See, for example (a) T. Manabe, T. Utsumi, and S. Okamura, *J. Polym. Sci.*, **58**, 121 (1962); (b) C. H. Bamford, A. D. Jenkins, and R. Johnston, *Trans. Faraday Soc.*, **55**, 1451 (1959); (c) A. Chapiro, M. Magat, J. Sebban, and P. Wahl, *Ric. Sci. Suppl.*, **25A**, 73 (1955); (d) P. E. M. Allen and C. R. Patrick, *Makromol. Chem.*, **47**, 154 (1961); (e) G. Henrici-Olivé and S. Olivé, *ibid.*, **37**, 71 (1960); (f) D. G. Smith, *J. Appl. Chem.*, **17**, 339 (1967).

(10) D. H. Johnson and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **74**, 938 (1952).

however, that our data implied that transfer to AIBN is not negligible. It is the purpose of this communication to report these data.

It will be worthwhile first to discuss the factors which affect determinations of the transfer constant of initiators and the reliability of such measurements. Clearly, the transfer constant of an initiator will be experimentally distinguishable from zero only if the third term in eq 1, transfer to the initiator, contributes a measurable fraction of the polymer end groups. As we shall see below, end-group formation by initiation usually outweighs that by transfer at low concentrations of initiator; it is at high initiator concentrations that transfer becomes important. For initiators which have very fast decomposition rates at the temperature used, it is possible that initiator concentrations high enough to lead to appreciable amounts of transfer cannot be conveniently attained.[14,15] Also, since primary radical termination becomes important at high rates, this additional chain-ending process may become important before transfer becomes significant.

Clearly, it is easier to measure the transfer constant of materials which are extremely poor initiators. In fact, the limiting case of an initiator which is fairly stable at the temperature of the measurements can be treated as if the initiator were an inert solvent, and the results are approximately correct.[16–18] For transfer to a species S, and where PRT is neglected, eq 1 becomes[19]

$$\frac{1}{\bar{P}} = \frac{k_t R_P}{k_p^2(\mathrm{M})^2} + C_M + C\frac{(\mathrm{S})}{(\mathrm{M})} \qquad (2a)$$

where k_t and k_p are the rate constants for termination and propagation, R_P is the rate of polymerization, C_M is the monomer transfer constant, C is the transfer constant of S, and (S) and (M) represent the molarities of S and the monomer. The first term in eq 2a gives chain ends due to initiation, the second those due to transfer to monomer, and the last those due to transfer to S. If the material S is not an initiator, then the ratio (S)/(M) can be varied without affecting R_P and the constants in eq 2a can be grouped into an over-all constant $1/\bar{P}_0$[19]

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + C\frac{(\mathrm{S})}{(\mathrm{M})} \qquad (2b)$$

Table I gives the values of $k_d f$ and the transfer constant C for several initiators in styrene at 60°. Both propyl and *t*-butyl peroxide are relatively stable at 60°. (They have half-lives for homolysis of about 10 years!) Although it was at one time thought that *t*-butyl peroxide had a transfer constant of zero, actually, as the table shows, both these dialkyl peroxides have small but finite values of *C*. These values would be experimentally indistinguishable from zero but for the extremely low rate of chain initiation by the dialkyl peroxides. In fact, the data can be treated as if the initiator were an inert solvent. We have discussed this in detail for the case of propyl peroxide;[16] the plot of $1/\bar{P}$ *vs.* (I)/(M) is a straight line as predicted by eq 2b and gives a value of C of 20×10^{-4}, very near the value given in Table I which is corrected for the change in R_P with changing values of (I). We also showed,[16] using the data of Mayo, Gregg, and Matheson,[15] that the plot of eq 2b for benzol peroxide does not give a straight line. For this initiator, $1/\bar{P}_0$ is a more sensitive function of the initiator concentration, and the plot of $1/\bar{P}$ *vs.* (peroxide)/(M) shows appreciable curvature. However, even here the limiting slope of the plot of eq 2b at very high peroxide concentrations gave a transfer constant of 0.10, again fairly close to the value of 0.055 shown in Table I.[16]

TABLE I
A COMPARISON OF VALUES OF $k_d f$ AND C FOR SEVERAL INITIATORS IN STYRENE AT 60°

Initiator	$k_d f$, sec^{-1}	C	Ref
Pr_2O_2[a]	2.7×10^{-9}	0.0008	16
t-Bu_2O_2[b]	1.5×10^{-9}	0.0006	17, 18
t-BuOOH[c]	5.0×10^{-10}	0.0350	10
Bz_2O_2[d]	1.9×10^{-6}	0.0550	15
AIBN	6.2×10^{-6}	0	10–13

[a] Di-*n*-propyl peroxide. [b] Di-*t*-butyl peroxide. [c] *t*-Butyl hydroperoxide. [d] Benzoyl peroxide.

t-Butyl hydroperoxide is an even slower initiator at 60° than is *t*-butyl peroxide. Some time ago, Tobolsky showed that for this initiator the plot of $1/\bar{P}$ *vs.* R_P is curved. The curvature in this plot for *t*-butyl hydroperoxide led Tobolsky to postulate transfer to this initiator, and this may be the first initiator for which transfer was recognized to be an important chain-ending process.[20] However, this plot is extremely insensitive to transfer; both benzoyl peroxide and AIBN appear to be similar and to give no transfer in this plot.[20] *t*-Butyl hydroperoxide has *both* a large transfer constant *and* a small value of $k_d f$; this combination makes it impossible to ignore transfer as an important chain-ending process.

In a classical and important contribution, Mayo[15] showed that it was possible to measure the transfer constant of benzoyl peroxide although it is an excellent initiator. It was necessary to use concentrations of the peroxide as large as 0.16 *M*, at which point about one-third of the chain ends arise from transfer to initiator. At low concentrations of peroxide only a negligible number of chain ends arise from transfer to the initiator.

The great similarity between benzoyl peroxide and

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(11) G. V. Schulz, G. Henrici-Olivé, and S. Olivé, *Z. Elektrochem.*, **60**, 296 (1956).

(12) N. G. Saha, U. S. Nandi, and S. R. Palit, *J. Chem. Soc.*, 12 (1958).

(13) J. C. Bevington and T. D. Lewis, *Polymer*, **1**, 1 (1960).

(14) For example, to measure the transfer constant of benzoyl peroxide, concentrations up to 0.16 *M* were studied (see ref 15). At this concentration of AIBN at 60°, the rate of conversion of styrene to polymer is nearly 10%/hr. It is difficult to start, stop, and control accurately the temperature of polymerizations at rates much beyond these. Furthermore, PRT already has become an important chain-ending process at this point. This is discussed in more detail below.

(15) F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Amer. Chem. Soc.*, 73, 1691 (1951).

(16) W. A. Pryor and E. P. Pultinas, *ibid.*, **85**, 133 (1963).

(17) W. A. Pryor, A. Lee, and C. E. Witt, *ibid.*, **86**, 4229 (1964).

(18) W. A. Pryor, *J. Phys. Chem.*, **67**, 519, 2889 (1963).

(19) See, for example, ref 4, p 245.

(20) B. Baysal and A. V. Tobolsky, *J. Polym. Sci.*, **8**, 529 (1952); also see ref 10. For an indication of the views at the time, see the discussion in ref 6, pp 134–136.

AIBN shown by the data given in Table I would make it appear that parallel studies of AIBN could test whether transfer occurs to this initiator as well. In fact, as we will show below, the slightly larger value of $k_d f$ and the slightly smaller value of C for AIBN make this task extremely difficult.

In a prelude to our study of primary radical termination in styrene, we decided to repeat the determination of the transfer constant of AIBN using tritium-labeled AIBN and the technique first used by Bevington.[18]

For a labeled initiator, I*, which contains a radioactive atom, the rate of incorporation of the label into the polymer can be described by Scheme I.[18] The

SCHEME I

$$\mathrm{I}^* \xrightarrow{k_d f} 2\mathrm{A}\cdot$$

$$\mathrm{A}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{AM}\cdot$$

$$\mathrm{AM}\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{AM}\cdot$$

$$\mathrm{AM}\cdot + \mathrm{I}^* \xrightarrow{k_{tr}} \mathrm{AMA} + \mathrm{A}\cdot$$

$$(\text{or} \xrightarrow{k_{tr}} \mathrm{AMH} + \mathrm{AA}\cdot)$$

$$\mathrm{A}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{AM}\cdot$$

$$(\text{or } \mathrm{AA}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{AAM}\cdot)$$

rate of incorporation of label into the polymer, R^*, which is one-half the rate of incorporation of A groups, R_A, is given by

$$R^* = {}^1/_2 R_A = {}^1/_2[2k_d f(\mathrm{I}^*) + 2k_{tr}(\mathrm{AM}\cdot)(\mathrm{I}^*)]$$

Substitution of the usual long-chain approximation for the radical concentration, $R_P = k_p(\mathrm{M}\cdot)(\mathrm{M})$, leads to eq 3, where R^* is the rate of incorporation of labeled

$$R^* = k_d f(\mathrm{I}^*) + \frac{C(\mathrm{I}^*)}{(\mathrm{M})} R_P \qquad (3)$$

initiator into the polymer, k_d and f are the unimolecular homolysis rate constant and efficiency for the initiator, C is its transfer constant, and (I*) and (M) are the molarities of the labeled initiator and the monomer. The concentration of labeled initiator and monomer are kept constant while R_P is varied by adding an unlabeled initiator. In this work we have used AIBN as both the labeled and the unlabeled initiator; this does not affect the validity of eq 3 but it allows the molecular weight of the polymer to be calculated from its activity. When R^* is plotted *vs.* R_P, a straight line should result with intercept $k_d f(\mathrm{I}^*)$ and slope $C(\mathrm{I}^*)/(\mathrm{M})$.

We have also measured the transfer constants for two model compounds for AIBN using the classical molecular weight technique[21] and eq 2b.

Experimental Section

[^{3}H]Acetone was prepared by stirring 8 ml of acetone with 0.2 g of sodum hydroxide and 30 ml of tritiated water (Nuclear Research Chemicals, 0.042 mCi/ml).

2,2′-Azobisisobutyronitrile (AIBN) was prepared by the method of Thiele and Heuser.[22] The corresponding hydrazo compound was prepared by mixing 10.4 g of hydrazine sulfate, 7.6 g of potassium cyanide, and 85 ml of water with the [^{3}H]acetone described above. The solution was allowed to stand for 36 hr. The resulting crystals were filtered, washed with water and dried in a vacuum desiccator.

TABLE II
CONTROLS FOR THE PURIFICATION OF LABELED AIBN POLYMER SAMPLES

Run	$R_P \times 10^4$ at which polymer was formed	Residual activity, dpm
1	0.82	20
2	1.86	30
3	3.53	36
4	4.77	27

The hydrazo compound was then dissolved in 50 ml of ethanol. To this solution was added 40 ml of 6 *N* hydrochloric acid and the hydrazo compound was oxidized with saturated bromine water until a permanent yellow color remained. The product was then precipitated and dried. It was then dissolved in ether, washed with concentrated hydrochloric acid and filtered to remove any unreacted hydrazo compound. The organic layer was removed and the product precipitated. The product was recrystallized twice from absolute ethanol (the temperature of which was not allowed to rise above 50°) and was dried in a vacuum desiccator. The yield was 3.2 g (28% from acetone) of AIBN-*t*, mp 104° (lit.[22] mp 105°), of specific activity 3.239×10^9 dpm/mol.

Tetramethylsuccinodinitrile was prepared by decomposing AIBN in refluxing toluene. The product was precipitated and recrystallized twice from absolute ethanol yielding tetramethylsuccinodinitrile with mp 168–169° (lit.[23] mp 167.0–167.5°). All other materials were purified in standard ways.[24]

Polymerization Techniques. The desired amount of tritium-labeled AIBN was placed in a volumetric flask and the flask was filled with styrene. This solution was transferred by volumetric pipet to glass ampoules containing a measured amount of unlabeled AIBN. The ampoules were deaired, sealed and placed in a 60 ± 0.01° bath for the desired length of time.[24] The ampoule contents were transferred to erlenmeyer flasks and freeze-dried to remove residual monomer. The individual polymer samples in about 20 ml of benzene were then precipitated four times using methanol at −10° and filtered through Whatman No. 2 filter paper.[25]

Controls were run to show that this polymer purification procedure is sufficient to remove most of the unreacted AIBN and its decomposition products from the polymer formed. Unlabeled polymer samples were prepared at four different rates of polymerization. A solution of labeled AIBN in benzene was sealed in an ampoule and placed in a 60° bath for 1 hr. The polymer samples were each mixed with an

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[21] R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947).

[22] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

[23] A. F. Bickel and W. A. Waters, *Rec. Trav. Chim. Pays-Bas*, **69**, 1490 (1950).

[24] W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Amer. Chem. Soc.*, **88**, 1199 (1966).

[25] Both the filter paper and methanol temperature have been found to be critical in maximizing the polymer recovery and in minimizing the amount of nonpolymeric, labeled products in the final polymer. Lower temperature methanol is more efficient for recovery of the polymer; however, AIBN is insoluble in cold methanol. Precipitations carried out under the conditions used here lead to polymer losses of less than 1% per precipitation.

TABLE III
THE POLYMERIZATION OF STYRENE INITIATED BY LABELED AIBN AT 60°

Point	(M)[a]	$(1^*) \times 10^3$[a,b]	Sec $\times 10^{-3}$	Vol,[a] ml	(I)[a] total	Amt of polymer, g	$10^3/\bar{P}$[c]	$R_P \times 10^4$	Polymer, dpm	$R^* \times 10^8$
1	7.91	3.93	21.48	8.27	3.93×10^{-3}	0.8144	0.506	0.44	12,832	2.23
2	7.90	3.92	10.68	8.29	1.56×10^{-2}	0.8030	1.04	0.87	6,538	2.28
3	7.89	3.92	10.68	8.29	1.78×10^{-2}	0.9177	1.02	1.00	6,454	2.25
4	7.87	3.91	7.08	8.32	3.59×10^{-2}	0.8870	1.45	1.45	4,369	2.29
5	7.83	3.89	5.28	8.36	6.48×10^{-2}	0.8607	2.05	1.87	3,319	2.32
6	7.76	3.85	4.20	8.42	9.98×10^{-2}	0.8761	2.58	2.38	2,760	2.41
7	7.72	3.83	3.48	8.47	1.38×10^{-1}	9.8416	2.42	2.74	2,293	2.40
8	7.62	3.78	3.00	8.58	2.09×10^{-1}	0.8915	4.02	3.33	2,093	2.51
9	7.52	3.73	2.58	8.69	2.78×10^{-1}	0.8833	4.72	3.78	1,829	2.52

[a] Average of initial and final values used. [b] The specific activity of the AIBN-*t* was 3.239×10^9 dpm/mol. [c] Calculated from the activity of the polymer.

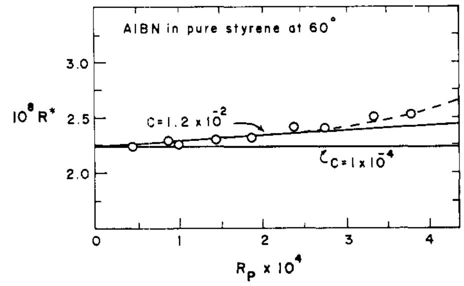

Figure 1. Graph of the rate of incorporation of radioactivity, R^*, *vs.* the rate of polymerization, R_P, for the AIBN-initiated polymerization of styrene at 60°. Lines are drawn showing slopes which yield transfer constants of 1.2×10^{-2} and 1×10^{-4}.

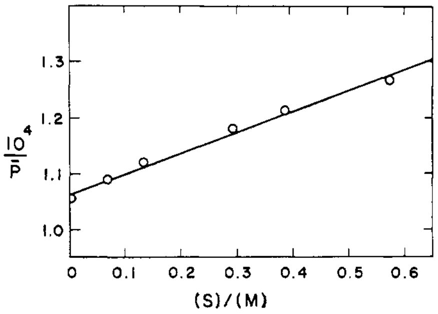

Figure 2. Graph of $1/\bar{P}$ *vs.* (S)/(M) for the thermal polymerization of styrene at 60° in the presence of tetramethylsuccinodinitrile.

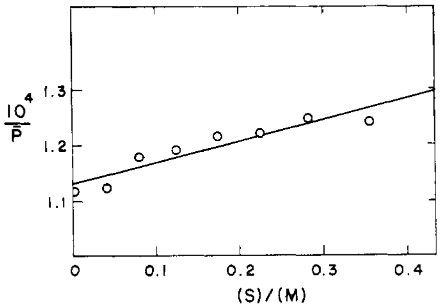

Figure 3. Graph of $1/\bar{P}$ *vs.* (S)/(M) for the thermal polymerization of styrene at 60° in the presence of trimethylacetonitrile (pivalonitrile).

amount of the AIBN solution containing the same amount of activity as used in kinetic runs. The polymer was then reisolated from these samples as described above. The results are presented in Table II. An average of 28 dpm was subtracted from the disintegrations per minute obtained for each polymer sample prepared using labeled AIBN.

Procedure for Counting Labeled Polymer Samples. A Packard Model 3365 Tricarb liquid scintillation counter was used. Efficiencies were determined by external standardization using acetone-quenched standards purchased from Packard.

Viscosity Molecular Weights. Experimental procedures have been previously described.[16,17,24] The number-average degree of polymerization was determined using eq 4.[15]

$$\frac{1}{\bar{P}} = \frac{6.2275 \times 10^{-4}}{[\eta]^{1.87}} \tag{4}$$

Calculation of R^* and R_P. Values of R^* and R_P were calculated as shown.

$$R^* = \frac{\text{(total dpm in polymer produced in run)}}{\text{(dpm/mol in AIBN used) (l.) (sec at 60°)}}$$

$$R_P = \frac{\text{(total g of polymer produced)}}{\text{(104.1) (l.) (sec)}}$$

Results

The results for the polymerization of styrene initiated by tritium-labeled AIBN are presented in Table III. Figure 1 shows a plot of these data in the form of eq 3; the line shown, which follows the points at low concentrations, indicates an apparent transfer constant for AIBN of $(1.2 \pm 0.2) \times 10^{-2}$. The deviation of the points at higher concentrations of AIBN reflects the inception of primary radical termination. (This is discussed below.)

A value for $k_d f$ of 5.7×10^{-6} is obtained from the intercept of Figure 1. This value is in only fair agreement with previously reported values,[9a,26-28] using classical techniques. However, it is in good agreement

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(26) The values obtained for $k_d f$ show dependence on the method used in its determination. For instance, from dead-end polymerization studies in styrene, $k_d f$ has been determined to be 8.5×10^{-6}.[27] Values from rate data include 6.7×10^{-6} and 7.9×10^{-6}.[9a,28]

(27) A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, *J. Amer. Chem. Soc.*, **82,** 1277 (1960);(b).

(28) D. H. Johnson and A. V. Tobolsky, *ibid.*, **74,** 938 (1952).

with the value of 6.4 × 10^{-6} obtained by Bevington and Lewis[18] using the tracer method employed here. Furthermore, if Bevington and Lewis had fitted their data to a finite value of C, then their value for k_df would agree with our value even more closely (see below).

In an effort to determine what would be a reasonable minimum value for the transfer constant of AIBN, the transfer constants of two model compounds, tetramethylsuccinodinitrile and pivalonitrile, were determined by the molecular weight technique. These data are presented in Figures 2 and 3; the two transfer constants were found to be 3.7 × 10^{-5} and 3.8 × 10^{-5}, respectively.

Table IV summarizes data for other model compounds from the literature. From these data, a lower limit of about 4 × 10^{-5} for the transfer constant of AIBN appears reasonable. (It might be noted from Figure 1 that this value would be indistinguishable from zero under the conditions used in this study.)

Table IV

Transfer Constants for Model Compounds

Compd	$C \times 10^4$	Ref
$(CH_3)_2\overset{\mathrm{CN}}{\overset{\vert}{\mathrm{C}}}—\overset{\mathrm{CN}}{\overset{\vert}{\mathrm{C}}}(CH_3)_2$	0.37	This paper
$(CH_3)_3CCN$	0.38	This paper
CH_3CN	0.44	26
$(CH_3)_3CCH_2CH_3$	0.4	*a*
$(CH_3)_3CPh$	0.06	21
CH_3SSCH_3	94	*a*
t-BuSSBu-*t*	1.4	*a*
BuSBu	22	*a*
t-BuSBu-*t*	250	*a*
t-BuOOBu-*t*	6	17, 18

[a] W. A. Pryor and T. L. Pickering, *J. Amer. Chem. Soc.*, **84**, 2705 (1962).

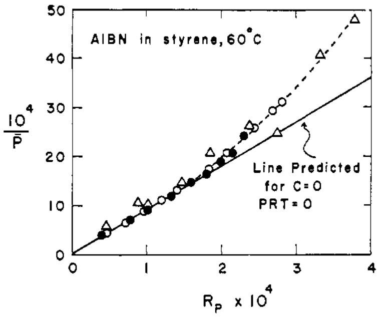

Figure 4. The polymerization of styrene initiated by AIBN at 60°; $1/\bar{P}$ *vs.* the rate of polymerization: ○, data of Manabe, Utsumi, and Okamura;[9a] ●, data for polystyrene samples with molecular weights determined viscometrically (data not presented in tables); △, our data taken from Table III with molecular weights calculated from the tritium activity of the polymer.

Discussion

A Comparison of the Transfer Constants of AIBN and Benzoyl Peroxide. It is clear, both from Figure 1 and from the model compounds in Table IV, that AIBN does not have a transfer constant of zero. In fact, the high reactivity of radicals makes it doubtful that any material will be found with a transfer constant identically equal to zero. Why then has the transfer constant of AIBN proven so difficult to measure? This question appears particularly puzzling if the value of 0.01 is entered in Table I as the transfer constant for AIBN; it then appears that AIBN and benzoyl peroxide have values of k_df and C which are extremely similar. Can these small differences make transfer to the former unambiguous and transfer to AIBN extremely difficult to measure?

The answer to this question can be shown to be "yes" in the following way. For a material which is an initiator at the temperature used, eq 2b will not give the correct transfer constant since R_P will be a function of the concentration of the initiator. Transfer to such an initiator must be computed as follows. The relation[29] between R_P and the concentration of the initiator is given by eq 5. If this relation is substituted into

$$R_P = k_p(\mathrm{M})(\mathrm{M}\cdot) = k_p(\mathrm{M})\left[\frac{k_df(\mathrm{I})}{k_t}\right]^{1/2} \tag{5}$$

eq 2a, eq 6 results.[16] (This expression was first derived and applied by Mayo[15] in a somewhat different form.)

$$\frac{1}{\bar{P}} = \frac{k_t^{1/2}}{k_p(\mathrm{M})}[k_df(\mathrm{I})]^{1/2} + C_M + C\frac{(\mathrm{I})}{(\mathrm{M})} \tag{6}$$

We recognize that the terms in eq 6 are those of eq 1, and we can add a term to eq 6 representing chain ends due to PRT (eq 7). If the values of k_df and C from Table

$$\frac{1}{\bar{P}} = \frac{k_t^{1/2}}{k_p(\mathrm{M})}[k_df(\mathrm{I})]^{1/2} + C_M + C\frac{(\mathrm{I})}{(\mathrm{M})} + \mathrm{PRT} \tag{7}$$

I are substituted into eq 7, eq 8 is obtained for the dependence of chain-end formation in the benzoyl peroxide initiated polymerization of styrene. (The value

$$\frac{10^4}{\bar{P}} = 48.6(\mathrm{Bz_2O_2})^{1/2} + 0.60 + 63.8(\mathrm{Bz_2O_2}) + \mathrm{PRT} \tag{8}$$

of $k_t^{1/2}/k_p$ has been taken[30] as 30, C_M as 0.60 × 10^{-4}, and (M) as 8.6.) A similar relation (eq 9) can be obtained for AIBN using the value of k_df in Table I and

$$\frac{10^4}{\bar{P}} = 87.0(\mathrm{AIBN})^{1/2} + 0.60 + 23.2(\mathrm{AIBN}) + \mathrm{PRT} \tag{9}$$

the upper limit value of 0.02 for the transfer constant taken from Figure 1. The number of chain ends due to primary radical termination for AIBN as the initiator can be estimated by the technique of Okamura.[9a] Figure 4 is a graph similar to that given by Okamura[31a] showing our data as well as his; the agreement is excellent.[31b] The deviation from the straight line can be used as an empirical measure of the number of chain ends due to PRT. It can be seen that at rates of polymerization below ~1.5 × 10^{-4} no chain ends are formed in this process, but the number increases quite

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(29) Reference 4, p 237.

(30) W. A. Pryor and G. L. Kaplan, *J. Amer. Chem. Soc.* **86**, 4234 (1964).

(31) (a) Figure 6 of reference 9a. (b) In Figure 4 we show the data taken from Table III in this paper (open triangles) as well as data from runs of ours which duplicate Okamura's work and for which molecular weights were determined viscometrically. (We have not given these data in tables.)

TABLE V
SOURCES OF CHAIN ENDS IN THE POLYMERIZATION OF STYRENE INITIATED BY BENZOYL PEROXIDE AT 60° CALCULATED USING EQUATION 8

		$(1/\bar{P}) \times 10^4$					% chain ends from	
(Bz_2O_2)	10^4R_P	Initiation	C_M	$C(I)/(M)$	PRT[a]	Total[b]	Transfer to initiator	PRT
10^{-4}	0.04	0.49	0.60	0.01	0	1.08	0.6	0
10^{-3}	0.13	1.54	0.60	0.06	0	2.17	2.7	0
5×10^{-3}	0.28	3.43	0.60	0.32	0	4.35	7.3	0
10^{-2}	0.40	4.86	0.60	0.64	0	6.10	10.5	0
10^{-1}	1.27	15.4	0.60	6.38	0	22.4	28.5	0
0.16	1.60	19.5	0.60	10.21	0.5	30.8	33.2	1.6

[a] Estimated from ref 9a. [b] The total values of $1/\bar{P}$ are fitted to the experimental data of ref 9a.

TABLE VI
SOURCES OF CHAIN ENDS IN THE POLYMERIZATION OF STYRENE INITIATED BY AIBN AT 60° CALCULATED USING EQUATION 9

		$(1/\bar{P}) \times 10^4$					% chain ends from	
AIBN	10^4R_P	Initiation	C_M	$C(I)/(M)$	PRT[a]	Total[b]	Transfer to to initiator	PRT
10^{-4}	0.07	0.87	0.60	0.002	0	1.54	0.13	0
10^{-3}	0.23	2.76	0.60	0.02	0	3.38	0.68	0
5×10^{-3}	0.51	6.15	0.60	0.12	0	6.87	1.7	0
1×10^{-2}	0.71	8.70	0.60	0.23	0	9.53	2.4	0
2×10^{-2}	1.01	12.3	0.60	0.46	0	13.4	3.4	0
4×10^{-2}	1.43	17.4	0.60	0.93	0	18.9	4.9	0
5×10^{-2}	1.60	19.5	0.60	1.16	0.5	21.7	5.3	2.3
8×10^{-2}	2.02	24.6	0.60	1.85	2.0	29.0	6.4	6.9
10×10^{-2}	2.27	27.5	0.60	2.32	3.0	33.4	6.9	9.0

[a] Interpolated from ref 9a. [b] The total $1/\bar{P}$ values are fitted to the experimental data in Table III.

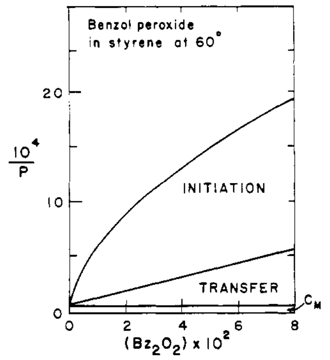

Figure 5. Sources of chain ends in the polymerization of styrene initiated by benzoyl peroxide at 60°. Lines are calculated from eq 8.

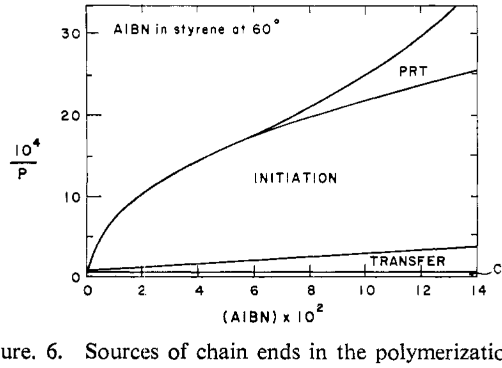

Figure. 6. Sources of chain ends in the polymerization of styrene initiated by AIBN at 60°. Lines are calculated from eq 9; the amount of primary radical termination (PRT) is estimated from Figure 4 as explained in the text.

steeply as the rate increases above this level. In the absence of data to the contrary, we will assume that PRT for the benzoyl peroxide initiated polymerization of styrene parallels that for AIBN; although this certainly is not exact, it will not be critical to our arguments.

Table V gives the calculated chain-end contribution for benzoyl peroxide initiated polymerizations using eq 8, and Figure 5 shows these sources of chain ends graphically. This figure is similar to that originally published by Mayo (Figure 7 of ref 15); however, he used the observed values of R_P to calculate chain ends due to initiation rather than computing them from the value of k_df. The agreementin the two figures is excellent, reflecting good choices for k_df, C, and $k_t^{1/2}/k_p$ in eq 8. Notice that it is only at very high concentrations of peroxide that transfer begins to account for an appreciate fraction of the end groups. Since the initiation term is parabolic in initiator and that in transfer is linear, high concentrations are required before transfer begins to overtake initiation as an important chain-end producing mechanism.

Table VI and Figure 6 show comparable data for AIBN calculated using eq 9. Notice that transfer never becomes an important chain-ending process for AIBN. Clearly, in studies of transfer to AIBN by the classical molecular weight method, the small fraction of the chain ends due to transfer might be overlooked. Transfer begins to become important only after PRT has become important, and PRT increases faster than does transfer as a chain-ending process as the concentration of AIBN is raised still further.

Nevertheless, it is clear from Table VI that *primary* *radical termination cannot be studied by the tracer technique* in the AIBN–styrene system at 60° *without allowing for chain ends due to transfer* by AIBN.

Solvent Effects on the Rate of Decomposition of AIBN. It is widely recognized that the rate of decomposition of benzoyl peroxide shows unusually strong solvent effects, whereas it is often stated that the decomposition of AIBN shows none. These facts are often interpreted as implying a pronounced induced decomposition for the peroxide and none for AIBN. Since transfer is an induced decomposition, this might imply that AIBN does not undergo transfer.

In fact, it has become increasingly clear in recent years that AIBN does show some dependency of its rate of decomposition on the nature of the solvent. For example, Olivé and Olivé have recently published the data reproduced in Table VII.[32a]

It is true that benzoyl peroxide shows a larger solvent effect on its rate of decomposition than does AIBN. In fact, benzoyl peroxide has an *unusually* sensitive dependence of the total rate of its decomposition on the nature of the solvent.[33] However, some of this rate effect is due to a solvent effect on the unimolecular rate constant k_d, some to variable amounts of induced decomposition, and some (in fact the most dramatic) to a concurrent ionic decomposition.[33] For example, the explosive decomposition of the peroxide in amines is at least partially due to an ionic mechanism.[34] In fact, if the total rates of decomposition for benzoyl peroxide are compared to values of k_d for AIBN for some of the solvents given in Table VII in which the ionic decomposition is probably of minor importance, the differences are not particularly pronounced. These data are shown in Table VIII. Clearly, the two rates do not parallel each other, but, in view of the complexities, this is not surprising. It would appear that the rate of decomposition of AIBN shows enough solvent dependence to conceal some contribution from an induced decomposition. The fact that the kinetics of decomposition of AIBN remain first order in all these solvents, although significant, does not rule out an induced path.[35]

TABLE VII
RATE CONSTANTS FOR THE DECOMPOSITION OF AIBN IN VARIOUS SOLVENTS AT 50°

Solvent	$k_d \times 10^6$, sec^{-1}
Cyclohexane	1.50
Dioxane	1.54
Butanone	2.06
Pyridine	2.06
Ethylbenzene	2.06
Benzene	2.18
Bromobenzene	2.61
Styrene	2.98

TABLE VIII
TOTAL RATES OF DECOMPOSITION OF BENZOYL PEROXIDE COMPARED WITH VALUES OF k_d FOR AIBN

Solvent	% decomposn in 1 hr Bz_2O_2[a]	$k_d \times 10^6$ AIBN[b]
Cyclohexane	51.0	1.5
Benzene	15.5	2.2
Ethylbenzene	15.0	2.1
Bromobenzene	26.3	2.6
Styrene	19.0	3.0

[a] Reference 33. [b] Reference 32a.

A Comparison of Our Results with Earlier Work. The elegant and original study of Bevington and Lewis[13] concluded that AIBN has a transfer constant which is "very close to zero" using the same tracer method which we have used here. These workers give a graph (their Figure 1) in which the grams of benzoyl peroxide or bis-3,5-dibromo-4-methoxybenzoyl peroxide which have been added to a solution of labeled AIBN in styrene are plotted *vs.* the function R_i. (Their R_i is equal to $2R^*$ in our notation.) Because of the fact that some AIBN is present in each of their runs, the amount of the peroxide added does not parallel R_P; also, of course, the two peroxides have different molecular weights and values of k_df. If this graph of R_i *vs.* added grams of inactive peroxide is converted into a graph of R^* *vs.* R_P, the effect is to compress greatly the scale of their x axis.[36] The total range of the R_P values for their six runs is 0.55–0.71 $\times 10^{-4}$; thus all their points would occupy an area on our Figure 1 of about the width of one of the circles on our graph. If all six of their data points are fitted to a straight line by least squares, a negative transfer constant of $(-1.4 \pm 18.0) \times 10^{-2}$ and a value of k_df of $(6.5 \pm 0.95) \times 10^{-6}$ sec^{-1} are obtained. (The errors cited are standard deviations.) Both points for the substituted peroxide and the last point for benzoyl peroxide fit the line extremely poorly, as is reflected by the standard deviation of the slope. However, the first three points with benzoyl peroxide as the inactive initiator do define a good straight line with positive slope. (This can be seen from the figure published by Bevington and Lewis.) If the results from these three benzoyl peroxide runs are fitted to a straight line, a positive value for the transfer constant of $(3.1 \pm 0.1) \times 10^{-2}$ and a value of k_df of $(6.17 \pm 0.06) \times 10^{-6}$ sec^{-1} are obtained. This is in reasonably good agreement with our results.

Possible Sources of Systematic Errors in Our Work. It is difficult to rationalize the much larger apparent transfer constant of AIBN obtained in Figure 1 and that of the model compounds given in Table IV. The model compounds indicate that methyl groups adjacent to a cyano group should lead to transfer

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(32) (a) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **58**, 188 (1962). Also see (b) J. E. Leffler, *et al.*, *J. Amer. Chem. Soc.*, **76**, 1425, 4169 (1954); *J. Org. Chem.*, **19**, 1089 (1954); (c) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961); (d) L. M. Arnett and J. H. Peterson, *ibid.*, **74**, 2031 (1952); (e) J. C. Bevington, *Makromol. Chem.*, **34**, 152 (1959); (f) A. F. Moroni, *ibid.*, **105**, 43 (1967).

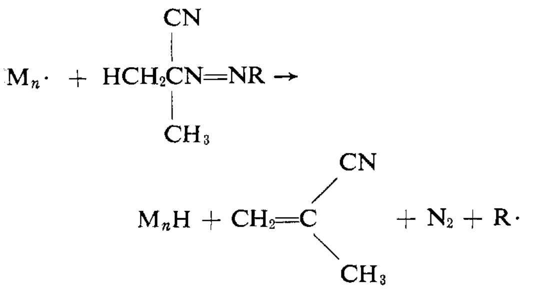
(33) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946).

(34) Reference 4, p 98.

(35) Reference 4, p 93. Also see G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 7127 (1965).

(36) We have converted the grams of peroxide added to R_P using k_df values for the substituted peroxide and benzoyl peroxide which were reported by Bevington (see ref 13). These values are AIBN, 6.4 $\times 10^{-6}$; benzoyl peroxide, 2.0 $\times 10^{-6}$; 3,5-dibromo-4-methoxybenzoyl peroxide, 9.5 $\times 10^{-7}$ sec^{-1} at 60°.

constants of the order of 5×10^{-5}, and, barring any special effects, the azo linkage would not affect this value significantly. However, special effects have been postulated before to rationalize enhanced transfer constants. For example, a synchronous β scission such as that shown in reaction 10 could lead to a significantly larger transfer constant in AIBN than for the less labile model compounds. A synchronous



$$\mathrm{M}_n\cdot + \mathrm{HCH_2}\overset{\mathrm{CN}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{N{=}NR} \rightarrow \mathrm{M}_n\mathrm{H} + \mathrm{CH_2{=}C}\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CH_3}\end{smallmatrix} + \mathrm{N_2} + \mathrm{R}\cdot$$

(10)

scission such as this was postulated to explain the transfer constant of *t*-butyl sulfide which is 10–100 times larger than expected.[37] (These data are shown in Table IV.) If this is the mechanism for transfer by AIBN, and if all the methacrylonitrile formed does not copolymerize and become incorporated into the polymer, then each transfer step incorporates only one-half of a labeled initiator. In this case, the true transfer constant is twice as large as that measured in Figure 1.

If the labeled AIBN copolymerized with styrene, either through the azo link or through the cyano groups, then the polymer would be active although chain transfer did not occur. In this case, the molecular weight method would give the correct transfer constant but the tracer method would not. We tested the possibility of polymerization through the cyano groups by allowing styrene to polymerize in the presence of tritium-labeled acetonitrile as solvent. In the presence of 12 vol % of the acetonitrile, the polymer was virtually totally inactive, consistent with a very small transfer constant and no copolymerization. However, in the studies on pivalonitrile shown in Figure 3, it was observed that solvent to monomer ratios approaching 0.45 lead to pronounced retardation of polymerization and to the formation of low molecular weight oils. These concentrations, however, are far greater than those of AIBN used. Thus copolymerization of AIBN probably does not occur through the cyano groups. Since the azo group bears substituents on both ends, it is doubtful if it would lead to copolymerization either.

About 20% of the AIBN decomposes in cage reactions which produce stable species, and it is possible that some copolymerization of these stable by-products could cause a spuriously large transfer constant to be observed.[38] In fact, Ayrey[39] proposed this explanation for the apparently large chain branching found at high conversions. This explanation can be ruled out, however. The runs at higher values of R_P were conducted for shorter times and less of the labeled by-products would be present. Thus this mechanism would lead to data giving a negative value of the transfer constant, and could not explain the high positive slope of Figure 1.

Implications of This Work on Measurements of Primary Radical Termination. As we have shown, the tracer technique is potentially a useful method for measuring the number of chain ends due to PRT. In order to obtain quantitative data using AIBN, we require a better estimate of the transfer constant of AIBN, and this is the goal of our present work. However, one positive result from our studies is already apparent. The method for measuring PRT suggested by Okamura[9a] is shown in Figure 4. In this method, a deviation in the plot of $1/\bar{P}$ *vs.* R_P is taken as the end groups due to PRT. However, transfer would produce the same type of deviation. Therefore, it is possible that Okamura, who assumed that AIBN has a transfer constant of zero,[40] has overestimated the number of end groups due to primary radical termination.

TABLE IX
FITTING OF THE DATA OF TABLE III TO EQUATION 3 USING LEAST SQUARES[a]

Points used	$C \times 10^2$	$k_d f \times 10^6$
1–5	1.18 ± 0.23	5.66 ± 0.04
1–6	1.70 ± 0.30	5.60 ± 0.06
1–7	1.61 ± 0.21	5.61 ± 0.05
1–8	1.86 ± 0.20	5.57 ± 0.05
1–9	1.85 ± 0.15	5.57 ± 0.04

[a] The data in Table III have been fit to eq 3: $R^* = k_d f(\mathrm{I}^*) + CR_P(\mathrm{I}^*)/(\mathrm{M})$. The slope and the standard deviation of the slope were then multiplied by (M)/(I*) or 2.013×10^3, and the intercept and its standard deviation were divided by (I*), or 3.90×10^{-3}, to obtain values of C and $k_d f$.

However, the following argument indicates that at least *some* of the deviation in Figures 4 and 6 must be due to PRT. We have *assumed* that the data shown in Figure 1 should not all lie on a single straight line because of the inception of PRT. However, an excellent straight line can be put through all nine of the data points shown and the transfer constant is essentially uneffected. Table IX gives these data. Since the *maximum* transfer constant of AIBN is approximately 0.02, and since Table VI and Figure 6 show that this transfer constant fails to account for all the end groups, some primary radical termination must be occurring.[41] The *quantitative* evaluation of the number of end groups due to PRT using this tracer technique must await a more reliable estimate of the value of the transfer constant for AIBN.[42]

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(37) See ref 28. Also see J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966).

(38) Reference 4, pp 129–132.

(39) G. Ayrey, *Chem. Rev.*, **63**, 645 (1963).

(40) T. Manabe, T. Utsumi, and S. Okamura, *J. Polym. Sci.*, **58**, 134 (1962); see ref 9a, p 134.

(41) Note that Figure 6 was constructed by predicting the number of end groups due to initiation, transfer to monomer, and transfer to AIBN as shown in eq 9, and then ascribing the difference between the sum of these end groups and the experimentally measured value to PRT. That is, the upper line in Figure 6 is fit to the experimentally observed values of $1/P$.

(42) NOTE ADDED IN PROOF. Since the submission of this paper [J. A. May, Jr., and W. B. Smith, *J. Phys. Chem.*, **72**, 2993 (1968)] have published a study of the styrene AIBN sys-

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]

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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 $2k_df/\delta^2$ 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).